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(71)Applicant : NEC CORP

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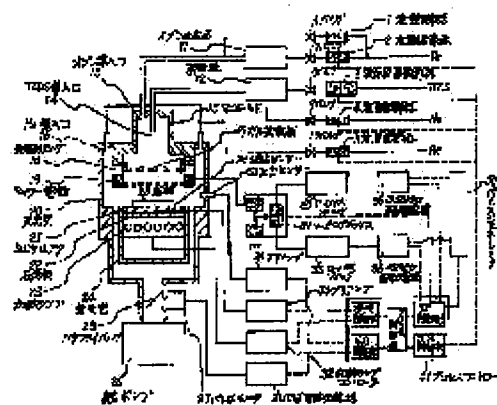
(72)Inventor : IKEDA YASURO

## (54) CHEMICAL VAPOR GROWTH, CHEMICAL VAPOR GROWTH DEVICE AND MANUFACTURE OF MULTILAYER WIRING

## (57)Abstract:

PURPOSE: To decrease water content contained in a coating film and to prevent the generation of the defective connection of through holes, through which a lower layer aluminum wiring and an upper layer aluminum wiring are connected to each other, by a method wherein organic silane and oxygen are contained in raw gas and while the intensity of plasma emission on the surface of a substrate is periodically changed, a desired thin film is formed.

CONSTITUTION: The flow rate of liquid organic silane is adjusted by a liquid flow rate adjuster 3. The liquid organic silane is completely vaporized by an evaporator 12, mixed with helium flowing at a flow rate adjusted by a flow rate adjuster 4, and organic silane gas is produced. Ozone-containing gas is produced by introducing oxygen supplied at a flow rate adjusted by a flow rate adjuster 2 in a silent discharge ozone generator 11. The produced organic silane gas and ozone-containing oxygen gas are introduced in a manifold 15. When the outputs of high-frequency power supplies 35 and 36 are changed in synchronizaton with a pulse, which is generated by a pulse generator 40, plasma between a shower electrode 19 and a substrate 28 is periodically changed to form a desired thin film. Accordingly, the amount of water content in an interlayer film is decreased and the crack resistance is enhanced.



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CLAIMS

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[Claim(s)]

[Claim 1]Plasma chemistry vapor phase growth forming a desired thin film changing periodically plasma irradiation intensity to the direction of a substrate including organic Silang and oxygen to at least a part of material gas.

[Claim 2]The chemical-vapor-deposition method according to claim 1 forming a desired thin film changing plasma irradiation intensity to a substrate face periodically including organic Silang and ozone content oxygen to at least a part of material gas.

[Claim 3]The plasma chemistry vapor phase growth according to claim 1 or 2 performing periodic change of said plasma irradiation intensity by repetition of a generation state of plasma and a non-generation state.

[Claim 4]The plasma chemistry vapor phase growth according to claim 1 or 2 performing periodic change of said plasma irradiation intensity by repetition of an exposure of plasma to a substrate face and un-glaring.

[Claim 5]A chemical vapor deposition apparatus comprising:

A mechanism which supplies organic Silang and oxygen to a wafer surface.

Oxygen plasma ion sources.

A shutter for changing plasma irradiation intensity periodically.

[Claim 6]It is a chemical-vapor-deposition method using organic Silang, oxygen, or ozone as material gas, A chemical-vapor-deposition method adding at least one kind in hydrogen peroxide ( $H_2O_2$ ), hydrogen ( $H_2$ ), water ( $H_2O$ ), hydrocarbon, alcohol, a carbonyl compound, and carboxylic acid furthermore.

[Claim 7]The chemical-vapor-deposition method according to claim 6 irradiating with plasma.

[Claim 8]The chemical-vapor-deposition method according to claim 7 forming a desired thin film changing plasma irradiation intensity to a substrate face periodically.

[Claim 9]The chemical-vapor-deposition method according to claim 9 performing periodic change of said plasma irradiation intensity by repetition of a generation state of plasma and a non-generation state.

[Claim 10]A manufacturing method of multilevel interconnection characterized by comprising the following.

It is organic Silang to material gas.

Ozone or oxygen.

A process of \*\*\*\*\*, hydrogen, water, hydrocarbon, alcohol, a carbonyl compound, and the carboxylic acid which adds one at least and at which only thickness more than height of metallic wiring forms an insulator layer on metallic wiring.

A process of forming flattening films, such as a resist film and organic silica membrane, and a process which carries out etchback by a reactive-ion-etching method.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the manufacturing method of a chemical-vapor-deposition method, a chemical vapor deposition apparatus, and multilevel interconnection.

[0002]

[Description of the Prior Art]The conventional plasma chemistry vapor phase growth formed the desired thin film on the processed board, using TEOS and oxygen for reactant gas, impressing the high-frequency power of a fixed output between the counterelectrodes in a reaction vessel, and generating the plasma of constant intensity.

[0003]The schematic diagram of the conventional plasma vapor phase growth system is shown in drawing 9.

[0004]The TEOS (tetraethyl orthosilicate) gas used as a silicon raw material carries out bubbling of the liquid TEOS131 put into the bubbler 132 by helium (helium) gas by which flow regulation was carried out by the flow regulator 123, evaporates TEOS, and is generated. Ozone content oxygen passes the ozone generator 165 for the oxygen gas by which flow regulation was carried out by the flow regulator 120, makes ozone of about 10% of concentration contain, and is generated. TEOS gas and ozone containing oxygen gas are introduced into the manifold 136 from the TEOS feed port 138, and oxygen and an ozone feed port 139, It is mixed within the manifold 136, and it hits the gas diffusion board 140, is spread, and distributes still more uniformly through the shower electrode 142, and the surface of the substrate 147 is sprayed. It is equipped on the SiC susceptor 144, optical heating is carried out from the heat lamp 146 through the quartz plate 145, and the substrate 147 is held at the temperature of about 350 \*\*. The shower electrode 142 is electrically insulated with other portions with the insulating ring 141.

The high frequency voltage of two frequency generated with 13.56-MHz RF generator 129 and the high-pass filter 130, 450-kHz RF generator 133, and the low pass filter 134 is impressed via the matching box 135.

The exhaust pipe 148 is connected to the vacuum pump 149, and the pressure of the reaction chamber 143 is held at the number Torr.

[0005]Usually, in the above devices, after spraying TEOS gas and the mixed gas of oxygen on the substrate 147 from the shower electrode 142 and checking the stability of a pressure etc. first, impress fixed high frequency voltage to the shower electrode 142, TEOS and oxygen are made to decompose, and a desired film is formed on the substrate 147.

[0006]In such a simple method, it turns out that the step coverage nature (step coverage) to the ground stepped surface of the formed film is bad (about 50%), and to perform plasma chemistry vapor phase growth, and ozone and the thermochemistry vapor phase growth of TEOS by turns is tried. When performing such a method to drawing 10, the change to the membrane formation time of the high-frequency power impressed to the shower electrode 142, the number of oxygen ion in plasma, and the ozone level in material gas is shown. Plasma

chemistry vapor phase epitaxy is performed, and the period when high-frequency power is impressed is performing ozone thermochemistry vapor phase epitaxy, although the number of oxygen ion shows the maximum. As for the period of zero, also in the number of oxygen ion, high-frequency power is zero.

After making high-frequency power into zero, in order to begin to pass ozone, fixed time is required by the time an ozone level rises. As mentioned above, when plasma chemistry vapor phase growth and ozone thermochemistry vapor phase growth are performed by turns, it is shown in drawing 11 (a) - (d) how a film is formed. On the aluminum wiring 153 formed on the substratum substrate, first, as shown in (b), the plasma CVD film 154 is formed. Next, as shown in (c), in order to embed the narrow space between aluminum wiring, 1st heat CVD film 155 is formed. As shown in (d), the 2nd plasma-CVD film 156 is formed. Such a process is repeated, film formation is performed to desired thickness, and the film of multilayer structure is formed like drawing 11 (d). It is important that ozone heat CVD film 155 remains in the form as it is by such a method especially. Because, if the film formation condition of ozone heat CVD film 155 is not proper, many moisture remains in a film, The problem that a steam blows off from the interlayer connection hole of aluminum wiring, exfoliation of an interlayer film arises with a steam, or the faulty connection (a poor through hole) in the interlayer connection hole of aluminum wiring occurs arises. It is known to these problems that it is effective to form ozone heat CVD film 155 on high ozone level conditions. However, under such high ozone level conditions, it is also known that the step coverage of ozone heat CVD film 155 on the 1st plasma-CVD film 154 will deteriorate. This is considered that the membranous quality of the 1st plasma-CVD film 154 happens since it differs on the upper surface and the side of the aluminum wiring 153.

[0007]Drawing 12 shows the formation method of the flattening insulator layer for multilevel interconnection which used conventional plasma chemistry vapor phase growth and the silica applying method. First, as shown in drawing 12 (a) and (b), only the thickness which is a grade where \*\* (void) is not made to the space between wiring forms the plasma-CVD film 159 on the aluminum wiring 158 formed on the substrate 157. Next, silica coating liquid is applied like drawing 12 (c), heat treatment of around 300 \*\* for 100 \*\* heat treatment for solvent evaporation and a membranous improvement is performed, and the silica coating film (1-time spreading) 160 is formed. The way things stand, since surface smoothness is insufficient, the process of silica spreading and heat treatment which were performed by drawing 12 (c) is repeated twice or more like drawing 12 (d), and the silica coating film (multiple-times spreading) 161 is formed. Etchback is carried out using the usual reactive-ion-etching method (RIE). Since an oxygen atom will be supplied from an oxide film if the plasma-CVD oxide film on aluminum wiring is exposed at this time, The etching rate of a silica coating film becomes large, and, as for the silica coating film 162 behind etchback, cratering the space part between aluminum wiring level differences is known like drawing 12 (e). Finally, again, the plasma-CVD film 163 is formed and an interlayer film is completed.

[0008]

[Problem(s) to be Solved by the Invention]The above-mentioned conventional plasma chemistry vapor phase growth had bad step coverage nature (step coverage), and was not able to lay the submicron space between aluminum wiring underground. In order to lay the submicron space between aluminum wiring underground, it is necessary to perform plasma chemistry vapor phase growth, and ozone and the thermochemistry vapor phase growth of TEOS by turns, or to form a silica coating film like drawing 12 like drawing 11, many times. However, the ozone TEOS heat CVD film formed under decompression of about 10 Torr and the silica coating film had much moisture contained in a film, there was a problem in opportunity intensity, an insulating property, etc., and there was a fault that the faulty connection of the through hole which connects lower layer aluminum wiring and the upper aluminum wiring especially arose. When membranes were formed on high ozone level conditions, the amount of film Nakamizu decreased, but step coverage deteriorated and there was fault where perfect embedding becomes impossible. In the method of carrying out etchback of a silica coating film like drawing 12 further again, the process of forming a silica coating film, and the process which carries out etchback were dramatically

complicated, and the increase in a routing counter and the fault of causing yield lowering also had it.

[0009]

[Means for Solving the Problem]A chemical-vapor-deposition method of this invention contains organic Silang, and oxygen or ozone as material gas, Furthermore, at least one kind in hydrogen peroxide ( $H_2O_2$ ), hydrogen ( $H_2$ ), water ( $H_2O$ ), hydrocarbon, alcohol, a carbonyl compound, and carboxylic acid is included. Plasma chemistry vapor phase growth of this invention forms a desired film, changing plasma irradiation intensity to a substrate face periodically including organic Silang, oxygen, or ozone content oxygen to at least a part of material gas. Under the present circumstances, repeat and perform a generation state and a non-generation state of plasma as a means to change plasma irradiation intensity, or. It repeats an exposure of plasma to a substrate face, and un-glaring, or high frequency voltage of two or more sorts of frequency is impressed to an electrode in a reaction vessel which counters, and high-frequency power of some or all of them is changed periodically.

[0010]A chemical vapor deposition apparatus of this invention is provided with the following.

A mechanism which supplies organic Silang.

A mechanism which supplies ozone content oxygen.

Hydrogen peroxide, hydrogen, water, hydrocarbon, alcohol, a carbonyl compound, a mechanism that makes a gaseous state at least one kind in carboxylic acid, and supplies it.

A chemical vapor deposition apparatus of this invention is provided with the following.

A mechanism which supplies organic Silang.

A mechanism which supplies oxygen or ozone content oxygen.

A mechanism to which plasma generation intensity is changed periodically, or several plasma irradiation mechanisms from which plasma strength provided in one reaction vessel differs.

A mechanism to which a substrate is moved among two or more of these plasma irradiation mechanisms.

A chemical vapor deposition apparatus of this invention is provided with the following.

A mechanism which supplies organic Silang and ozone content oxygen to a wafer surface.

Oxygen plasma ion sources.

A mechanical or electromagnetic shutter for changing plasma irradiation intensity periodically.

A chemical vapor deposition apparatus of this invention impresses high frequency voltage of two or more sorts of frequency to an electrode in a reaction vessel which counters, and has a mechanism to which high-frequency power of some or all of them is changed periodically.

[0011]A manufacturing method of multilevel interconnection of this invention to material gas Organic Silang, Including ozone or oxygen, further by a chemical-vapor-deposition method of hydrogen peroxide, hydrogen, water, hydrocarbon, alcohol, a carbonyl compound, and the carboxylic acid which adds one at least. A process at which only thickness more than height of metallic wiring forms an insulator layer on metallic wiring, a process of forming flattening films, such as a resist film and organic silica membrane, and a process which carries out etchback by a reactive-ion-etching method are included. A process at which a manufacturing method of multilevel interconnection of this invention makes organic Silang, ozone, or oxygen material gas, plasma irradiation intensity to a substrate face is changed periodically, and only thickness more than height of metallic wiring forms an insulator layer on metallic wiring, A process of forming flattening films, such as a resist film and organic silica membrane, and a process which carries out etchback by a reactive-ion-etching method are included.

[0012]

[Example]Next, this invention is explained with reference to drawings.

[0013]Drawing 1 is outline drawing of longitudinal section of the plasma chemistry vapor phase growth system showing the 1st example of this invention.

Drawing 2 expresses operation of a plasma chemistry vapor-phase-epitaxy difference of drawing 1 about the

temporal change of impression high-frequency power, the number of oxygen ion, and an ozone level, and drawing 3, Are the outline of the principle of this invention a model figure which expresses, and drawing 4, the time of being drawing of longitudinal section showing the growth process of the time progress and the film at the time of performing operation like drawing 2, and drawing 5 performing operation like drawing 2 -- high frequency ON time ( $t_{ON}$ ) -- the relation of a film growth rate, step coverage, and the absorption index of an OH radical is shown comparatively (duty D).

[0014]Drawing 1 is outline drawing of longitudinal section of the plasma chemistry vapor phase growth system of Example 1 of this invention. In the device of this example, the ethyl silicate (it calls the following TEOS) gas used as a silicon raw material, Carry out flow regulation of the liquid TEOS supplied from the TEOS tank which is not expressed with this figure with the mass flow type liquid flow rate regulator 3, and it is made to evaporate thoroughly by evaporation term 12, and it is mixed with the helium by which flow regulation was carried out by the flow regulator 4, and is generated. Ozone content oxygen introduces into the silent discharge type ozone generator 11 the oxygen by which flow regulation was carried out by the flow regulator 2, makes 1 to 10% of ozone contain, and is generated. Thus, the TEOS gas and ozone containing oxygen gas which were generated are introduced into the manifold 15 from the TEOS feed port 14 and the ozone feed port 13. Within a manifold, it is mixed and these gases are diffused almost uniformly by hitting the gas diffusion board 17. If it hits the shower electrode 19, it will distribute still more uniformly and the surface of the substrate 28 will be sprayed. It is equipped on the SiC susceptor 21, optical heating is carried out from the heat lamp 23 through the quartz plate 22, and the substrate 28 is held at the temperature of about 200-450 \*\*. The shower electrode 19 is electrically insulated with other portions with the insulating ring 18.

The high frequency voltage of two frequency generated with the source 36 and the low pass filter 35 is impressed via the matching box 37 by 13.56-MHz RF generator 39 and the high-pass filter 38, and 450-kHz high frequency. The exhaust pipe 24 is connected to the vacuum pump 26, and the pressure of the reaction chamber 20 is held at 0.1 - tens Torr(s).

[0015]The mixer part which mixes the high frequency voltage of two frequency inside the matching box 37 connected to the shower electrode 19 in this example, There are a matching part which performs an impedance match, a dummy load, and a solid state switch, and the high frequency voltage impressed to the shower electrode 19 can be turned now on and off. It is also possible to change the output of RF generators 35 and 36 and to change the high frequency voltage impressed to the shower electrode 19 synchronizing with PASURU which the pulse generator 40 generates. These operations are controlled by the process controller 41 including substrate temperature, a reaction chamber pressure, etc. Transfer ways, such as these control signals, pulses, etc., are shown by the dashed line in drawing 1.

[0016]Here, operation of this device at the time of turning on and off the high frequency voltage impressed to the shower electrode 19 in periodic 1 second is explained using drawing 2, drawing 3, drawing 4, and drawing 5.

[0017]The drawing 2 \*\*\*\*\* shows the relation between membrane formation time and high-frequency power. Plasma occurs between the shower electrode 19, the substrate 28, or the SiC susceptor 21 between time  $t_{ON}$  from which high-frequency power is turned on, and oxygen or ozone decomposes and it is generated by oxygen ion. The drawing 2 middle expresses change of the number of oxygen ion. Since it begins to impress high-frequency power, by the time the plasma state is stabilized, a certain fixed time will be required and will have become a waveform with sloping shoulders. Since ozone is more unstable than oxygen, the ionization efficiency by impression of high-frequency power is high. Therefore, like the drawing 2 upper row, the number of ozone molecules in plasma falls considerably, when high-frequency power is one.

[0018]Drawing 3 (a) and (b) is a model figure showing the situation near [ at the time of high frequency one and

OFF ] the substrate face, respectively. Plasma occurs between the shower electrode 19 of drawing 1, and the substrate 28 at the time of high frequency ion. In plasma, an oxygen molecule and a TEOS molecule dissociate in the electron 45, the oxygen ion 47, the TEOS dissociation molecule 46, and oxygen radical 55 grade. Sheath voltage occurs between plasma and a substrate, it is accelerated with this voltage, and the drift of the oxygen ion 47 is carried out, and it collides with a substrate face. The TEOS dissociation molecule 46 is also diffused toward a substrate face, and it becomes the film formation precursor 50 by a pyrolysis or decomposition by an oxygen ion shock in a formation membrane surface. It reacts to an oxygen radical etc. in a formation membrane surface, and the formation film 51 is formed. Under the present circumstances, since very many oxygen ion shocks are shown in the surface of the formation film 51, the life of the film formation precursor 50 is quite short, and the density in a formation membrane surface is low. An oxygen ion shock has the operation which stiffens the formation film 51, and membraneous quality is good and is useful for formation of the film of compression stress.

[0019]Now, once high frequency is come by off (refer to drawing 3 (b)), an electron and the number of oxygen ion will decrease promptly, but the TEOS dissociation molecule 46 and the oxygen radical 55 remain still more. These are diffused on the surface of the formation film 51, serve as the film formation precursor 50, and decrease soon. It is spread toward a membrane surface, and the TEOS molecule 54 and the ozone molecule 56 also react, and serve as a TEOS dissociation molecule and a film formation precursor. In the surface of the formation film 51, since a film formation reaction is only thermal reaction, a film formation precursor exists in a formation membrane surface by high density, and the film formation precursor pseudo-liquid layer 59 is formed in it. The thickness of the side lower part of the level difference currently formed in the substrate 52 becomes thick, and this film formation precursor pseudo-liquid layer 59 eases inclination on the level difference side in order to show the character of a fluid.

[0020]Drawing 4 is drawing of longitudinal section showing time progress when high-frequency power is impressed like drawing 2, and the situation of film formation in model. First, like drawing 4 (a), high frequency is turned on between time  $t_{ON}$  (drawing 2 0.5 second), and 1st about 10-nm plasma-CVD film 60 is formed. Next, 1st heat CVD film 62 is formed between time  $t_{OFF}$  (0.5 second) like drawing 4 (b). Time  $t_{OFF}$  is dramatically as short as 0.5 second, and the thickness of 1st heat CVD film 62 is about 1 nm. Therefore, refining will be carried out with an oxygen ion shock etc. in early stages of the next  $t_{ON}$ , and it will be membraneous quality equivalent to a plasma-CVD film. Therefore, like drawing 4 (c), the 1st plasma-CVD film 60 and distinction stop attaching 1st heat CVD film 62 by which refining was carried out, and it will be incorporated into the 1st plasma-CVD film 60. Since a heat CVD film is an effect of a film formation precursor pseudo-liquid layer, the angle of the narrow space between wiring or the level difference lower part can be embedded and shape can be made smooth, It means forming the formation film 64 before the 2nd plasma-CVD film growth of membraneous quality equivalent to plasma CVD in shape equivalent to the heat CVD by the continuing plasma irradiation in early stages of plasma-CVD film growth. Since the level difference lower part has roundish shape with the formation film 64 before the 2nd plasma-CVD film growth, the shape of the 2nd plasma-CVD film 63 formed on this is also roundish like drawing 4 (c). In order that distinction may not attach the formation film 64 before the 2nd plasma-CVD film growth, and the 2nd plasma-CVD film 63, either, in the growth step (d) of 2nd continuing heat CVD film 65, a lower layer film turns into the formation film 66 after the 2nd plasma-CVD film growth.

[0021]By repeating the above stages many times, like drawing 4 (e), there is no \*\* (void) in the space part between the aluminum wiring 61, and the formation film of good membraneous quality almost equivalent to a plasma-CVD film can be embedded.

[0022]Drawing 5 shows the relation between the value of duty ratio  $D (D=t_{ON}/(t_{ON}+t_{OFF}) \times 100 (\%))$  calculated from  $t_{ON}$  and  $t_{OFF}$  in drawing 2, and the absorption index of the OH radical in a growth rate, step coverage, and a



film. The drawing 5 bottom shows that a growth rate increases, so that D is large, and it turns out that step coverage will begin to get worse if D exceeds 50%, and discontinuation shows becoming small enough, if, as for an OH radical, D exceeds 40% from the upper row. Although step coverage and a film Nakamizu daily dose (OH radical absorption index in a film) tend to conflict from drawing 4, by setting a duty ratio D value as the suitable range (it is 40 to 60% in the case of this example) shows that both can be prevented from spoiling.

[0023]Although the ethyl silicate (TEOS: chemical formula  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) was used as organic silane gas in this example, A tetramethylsilane (TMS: chemical formula  $\text{Si}(\text{CH}_3)_4$ ), Tetramethyl cyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS), The same result is obtained even if it uses silicon containing compounds, such as hexamethyldisilazane (HMDS), triethoxysilane ( $\text{SiH}(\text{OC}_2\text{H}_5)_3$ ), and a tris dimethylamino silane ( $\text{SiH}(\text{N}(\text{CH}_3)_2)_3$ ).

[0024]Since the life of an oxygen radical or a TEOS dissociation molecule is quite long even if ozone in reactant gas does not exist, the same result will be obtained if the value of duty ratio is chosen suitably. The same result is obtained also when hydrides and organic compounds, such as nitrogen compounds, such as silicon inorganic compounds, ammonia, etc., such as Silang, Lynn, boron, arsenic, antimony, are made to mix into reactant gas.

[0025]Although only the high-frequency power impressed to the shower electrode 19 was changed by this example further again, if high-frequency power, a reaction chamber pressure, substrate temperature, a gas mass flow, etc. are changed synchronizing with the pulse which the pulse generator 40 generates, better step coverage nature will be obtained.

[0026]Drawing 6 (a) is an outline top view of the reaction chamber of the plasma chemistry vapor phase growth system of the 2nd example of this invention.

Drawing 6 (b) is drawing of longitudinal section which met the A-A' line of drawing 6 (a).

Drawing 6 (a) expresses the top view which met the B-B' line of drawing 6 (b).

[0027]The reaction chamber 72 is divided into the field of six fanning, and fanning of the direction of 3:00 of a clock has become the heat CVD field 70.

Clockwise, it is arranged a plasma-CVD field, a heat CVD field, the plasma-CVD field 166, and by turns.

It is equipped with the substrate 69 on the susceptor 71 which rotates the axis of rotation 79 as an axis, and it passes through a heat CVD field and a plasma-CVD field by turns.

[0028]After TEOS gas and ozone content oxygen are introduced into the heat CVD field 70 and it distributes uniformly with the gas distribution plate 83 and the shower injector 81 from the TEOS feed port 73 and the ozone feed port 75, the surface of the substrate 69 is supplied to it. Since the substrate 69 is heated by about 350 °C with the heater 80 installed in the back side of the susceptor 71, the heat CVD film by ozone and TEOS grows on a substrate.

[0029]TEOS gas and oxygen gas are introduced into the plasma-CVD field 166 from the TEOS feed port 73 and the oxygen feed port 74, it is uniformly distributed by gas distribution plate 83' and the shower electrode 78, and the surface of substrate 69' is supplied. The shower electrode 78 is electrically insulated from other portions of the reaction chamber by the insulating ring 82 and the insulator 76.

The high frequency voltage of 13.56 MHz or 450 kHz is impressed from RF introduction terminal 77.

Between the shower electrode 78, substrate 69', or the susceptor 71, plasma is excited by impression of such high frequency voltage, and a plasma-CVD film is formed.

[0030]As mentioned above, in order that the substrate 69 may pass through a plasma-CVD field and a heat CVD field by turns with the rotating susceptor 71, a plasma-CVD film and a heat CVD film are formed by turns. Under the present circumstances, if revolving speed of the susceptor 71 is made into a per minute 10 rotation grade, the thickness of the heat CVD film formed in the heat CVD field 70 is set to about 2 nm, plasma irradiation will be

carried out in early stages of membrane formation of a \*\*\*\*\* plasma-CVD field, and membraneous quality will become being the same as that of a plasma-CVD film. Thus, as drawing 4 described, membraneous quality is the same as that of a plasma-CVD film, and the CVD film excellent in step coverage and level difference embedding nature is formed.

[0031]Although the reaction chamber was divided into six fields, this example will be available for it without limit, if this is two or more. Although the kind of film forming zone was made into two kinds, a heat CVD field and a plasma-CVD field, two or more sorts may be provided with the frequency and applied power of high frequency which impress a plasma-CVD field.

[0032]Although the susceptor 71 was made into the shape of a plane turntable and the shower injector and the shower electrode were provided up in this example, a susceptor is made into a cylinder or the shape of a multiple pillar, the lateral surface is equipped with a substrate, and the same result is obtained, even if it counters with a substrate and provides a shower electrode etc.

[0033]Although the ethyl silicate (TEOS: chemical formula  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) was used as organic silane gas in this example, A tetramethylsilane (TMS: chemical formula  $\text{Si}(\text{CH}_3)_4$ ), Tetramethyl cyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS), Hexamethyldisilazane (HMDS), triethoxysilane (chemical formula  $\text{SiH}(\text{OC}_2\text{H}_5)_3$ ), The same result is obtained even if it uses silicon containing compounds, such as a tris dimethylamino silane (chemical formula  $\text{SiH}(\text{N}(\text{CH}_3)_2)_3$ ).

[0034]Since the life of an oxygen radical or a TEOS dissociation molecule is quite long even if ozone does not exist in reactant gas, the same result will be obtained if the value of duty ratio is chosen suitably. The same result is obtained also when hydrides and organic compounds, such as nitrogen compounds, such as silicon inorganic compounds, ammonia, etc., such as Silang, Lynn, boron, arsenic, antimony, are made to mix into reactant gas.

[0035]Drawing 7 is a gross section figure showing the outline of the plasma chemistry vapor phase growth system of the 3rd example of this invention.

[0036]The argon gas Ar by which flow regulation was carried out to oxygen gas  $\text{O}_2$  by which flow regulation was carried out to the ion source cave 93 by the flow regulator 103 by the flow regulator 87 is supplied, and the pressure is maintained at  $p=1\text{mTorr}$ . Microwave with a frequency of 2.54 GHz is supplied via the waveguide 85 and the transmission window 86 from the microwave power supply 84. By the 875 gauss magnetic field which the main electromagnet coil 94 makes, within the ion source cave 93, the electron cyclotron resonance (ECR) has happened and the high oxygen plasma of an ionization rate occurs. With the emission magnetic field and the auxiliary coil 96 of the main electromagnet coil 94, oxygen ion is pulled out to the reaction chamber 95, and it is irradiated with it to the substrate 106. The TEOS gas used as a silicon raw material carries out flow regulation of the TEOS gas which evaporated from TEOS111 kept warm in the homoiothermal container 112 kept at 80 \*\* by the flow regulator 113, and is introduced from the TEOS feed port 107 to a reaction chamber. The oxygen gas by which flow regulation was carried out with the flow regulator 101 passes the ozone generator 98, becomes ozone content oxygen, and is supplied from the ozone feed port 97. It is equipped with the substrate 106 on the susceptor 109, and it is heated by 300 \*\* with the heater 110. Flow regulation of the pressure of a reaction chamber is carried out by the flow regulator 88, and it is maintained at about 1 mTorr by the argon gas for dilution and the vacuum pump 105 which are supplied from the Ar feed port 108.

[0037]In the plasma CVD device of this example, oxygen plasma is first generated in the ion source cave 93. It is suitable, and it comes out, and is made the small value, and the exposure of oxygen plasma makes the auxiliary coil 96 and the current sent through 96' the grade which generates the magnetic field which faces to a substrate from an ion source and which becomes uniform. The magnetic field which faces to a substrate is generated, and it is suitable, and comes out from an ion source, and the current sent through reflective magnetic coil 102,102' is

also made into the small value. If the substrate 106 surface is made to irradiate with oxygen ion and TEOS gas is supplied in this state, ECR plasma vapor phase epitaxy will happen and the good plasma-CVD film of membraneous quality will be formed. About 10 nm is formed. Next, the value of the current sent through the auxiliary coil 96 and 96' is strengthened, a mirror type magnetic field is formed near an ion source cavernous exit, and it is made for the electron and ion which flow out of plasma by the main electromagnet coil 94 and the emission magnetic field of 94' to rebound. Then, on the substrate 106, only neutral particles diffused from TEOS gas and an ion source, such as an oxygen radical and an oxygen molecule, are supplied, only a heat CVD reaction occurs, and good membrane formation of step coverage is performed. Then, if the auxiliary coil 96 and the current sent through 96' are changed with the cycle of 1 to about 10 seconds, The number of oxygen ion irradiated by the substrate 106 changes periodically, a plasma-CVD film and a heat CVD film are formed by turns, further, refining to the plasma-CVD film of a heat CVD film is also performed, and the plasma CVD excellent in step coverage and level difference embedding nature is formed like drawing 4. Since the reaction chamber pressure is especially set to about 1 mTorr by this example, a winning popularity lump of the big slot on the aspect ratio also becomes possible.

[0038]Although the mirror type magnetic field formed with the auxiliary coil 94 was used in the above-mentioned example as a means to change the oxygen ion irradiated by the substrate 106, The cusp type magnetic field formed of reflective magnet 102,102' and the recoil electric field formed in the susceptor 109 by impressing positive voltage may be used. Although not shown in drawing 7, the same result is obtained even if it uses an opportunity shutter. However, when it is made structure which bars diffusion of an oxygen radical using a mechanical shutter etc., it cannot be overemphasized that it is better to operate the ozone generator 98, to supply ozone near the substrate, to promote thermochemistry vapor phase epitaxy, and to have promoted growth of the heat CVD film.

[0039]In the above-mentioned example, although the electron cyclotron resonance type (ECR) ion source was used as an ion source, if the intensity of oxygen ion can be changed, it will not be based on the form but the same result will be obtained.

[0040]Although the ethyl silicate (TEOS: chemical formula  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) was used as organic silane gas in this example, A tetramethylsilane (TMS: chemical formula  $\text{Si}(\text{CH}_3)_4$ ), Tetramethyl cyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS), Hexamethyldisilazane (HMDS), triethoxysilane (chemical formula  $\text{SiH}(\text{OC}_2\text{H}_5)_3$ ), The same result is obtained even if it uses silicon containing compounds, such as a tris dimethylamino silane (chemical formula  $\text{SiH}(\text{N}(\text{CH}_3)_2)_3$ ).

[0041]The same result is obtained also when hydrides and organic compounds, such as nitrogen compounds, such as silicon inorganic compounds, ammonia, etc., such as Silang, Lynn, boron, arsenic, antimony, are made to mix into reactant gas.

[0042]Drawing 8 is drawing of longitudinal section showing the interlayer insulation film flattening method of the 4th aluminum multilevel interconnection of this invention.

[0043]In this example, the aluminum wiring 114 is first formed on the substrate 115 in which the semiconductor device etc. were formed (drawing 8 (a)). Next, using the plasma chemistry vapor phase growth system of Example 1 of this invention, among a figure, as shown in (b) and (c), CVD film 116 of this invention is formed more thickly than the thickness of aluminum wiring. Postbake of the resist 117 is applied and carried out. Etchback is performed and it is made for the surface of a CVD film to become flat using the reactive-ion-etching method adjusted so that the etching rate of CVD film 116 of the resist 117 and this invention might become equal. Then, the interlayer film 118 by which flattening was carried out is done.

[0044]In this example, although resist was used for flattening, even if it uses polyethylene, organic SOG, etc., an

equivalent result is obtained. As a flattening method, if grinding method is used, it will cross to an entire substrate and good surface smoothness will be obtained.

[0045]Drawing 13 shows the method of the operation of the 5th example which uses the plasma chemistry vapor phase growth system of Example 1 of drawing 1. It expresses with drawing 13 about 13.56-MHz high-frequency power, 450-kHz high-frequency power, ion current density, and average ion energy. However, any value is standardized at the maximum of each value.

[0046]In the method of operation of this example, like the 1st step and the 2nd step from under drawing 13, As a pulse is sent to RF generators 39 and 36 of two frequency (13.56 MHz and 450 kHz) of drawing 1 from the pulse generator 40 and the maximum output of the high frequency of two frequency becomes an opposite phase to them, voltage is impressed to the shower electrode 19. Then, like the 3rd step and the 4th step from under drawing 13, although change of ion current density is small, average ion energy takes the maximum, when 450-kHz high-frequency power is the maximum, and when 13.56-MHz high-frequency power is the maximum, it can serve as the minimum. If this has the high frequency of the high frequency to impress, it will be because the voltage (sheath voltage) produced between plasma and a substrate decreases. Thus, in that the intensity of an ion bombardment changes periodically, and does not have degradation of membraneous quality, and step coverage nature and slot embedding nature are improved, when changing only ion energy, although it is the same as that of Example 1, without changing ion current density, Like the drawing 13 highest rung, there is an advantage that change of a film growth rate can be small performed to about 10%.

[0047]In this example, although the device of drawing 1 was used, even if it uses the device of drawing 6 and drawing 7 which were shown in other examples of this invention, the same result can be obtained.

[0048]Although the ethyl silicate (TEOS: chemical formula  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) was used as organic silane gas in this example, A tetramethylsilane (TMS: chemical formula  $\text{Si}(\text{CH}_3)_4$ ), Tetramethyl cyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS), Hexamethyldisilazane (HMDS), triethoxysilane (chemical formula  $\text{SiH}(\text{OC}_2\text{H}_5)_3$ ), The same result is obtained even if it uses silicon containing compounds, such as a tris dimethylamino silane (chemical formula  $\text{SiH}(\text{N}(\text{CH}_3)_2)_3$ ).

[0049]Since the life of an oxygen radical or a TEOS dissociation molecule is quite long even if ozone does not exist in reactant gas, the same result will be obtained if the value of duty ratio is chosen suitably. The same result is obtained also when hydrides and organic compounds, such as nitrogen compounds, such as silicon inorganic compounds, ammonia, etc., such as Silang, Lynn, boron, arsenic, antimony, are made to mix into reactant gas.

[0050]Although only the high-frequency power impressed to the shower electrode 19 was changed by this example further again, if high-frequency power, a reaction chamber pressure, substrate temperature, a gas mass flow, etc. are changed synchronizing with the pulse which the pulse generator 40 generates, better step coverage nature will be obtained.

[0051]Drawing 14 is outline drawing of longitudinal section of the plasma chemistry vapor phase growth system of the 6th example of this invention. In the device of this example, the ethyl silicate (it calls the following TEOS) gas used as a silicon raw material, Carry out flow regulation of the liquid TEOS supplied from the TEOS tank which is not expressed with this figure with the mass flow type liquid flow rate regulator 175, and it is made to evaporate thoroughly with the evaporator 187, and it is mixed with the helium by which flow regulation was carried out by the flow regulator 176, and is generated. Ozone content oxygen introduces into the silent discharge type ozone generator 186 the oxygen by which flow regulation was carried out by the flow regulator 174, makes 1 to 10% of ozone contain, and is generated. Hydrogen peroxide gas is generated by carrying out bubbling of the fluid hydrogen peroxide 185 in the homoiothermal container 177 with the helium by which flow regulation was carried out by the flow regulator 177. Although the concentration of hydrogen peroxide gas was adjusted at the

temperature of the homoiothermal container 184, it was used in 10-20 \*\* at this example. Thus, the TEOS gas, ozone containing oxygen gas, and hydrogen peroxide gas which were generated are introduced into the manifold 208 from the TEOS feed port 189, the ozone feed port 188, and the hydrogen oxide gas inlet 190. Within a manifold, it is mixed and these gases are diffused almost uniformly by hitting the gas diffusion board 192. If it hits the shower electrode 194, it will distribute still more uniformly and the surface of the substrate 207 will be sprayed. It is equipped on the SiC susceptor 196, optical heating is carried out from the heat lamp 198 through the quartz plate 197, and the substrate 207 is held at the temperature of about 200-450 \*\*. The shower electrode 194 is electrically insulated with other portions with the insulating ring 193.

The 13.56-MHz high frequency generated with RF oscillator 206 is impressed.

The exhaust pipe 199 is connected to the vacuum pump 201, and the pressure of the reaction chamber 195 is held at 0.1 - tens Torr(s).

[0052]The above devices are used in this example, The insulator layer was formed by the film formation condition of the forming temperature of 200 \*\*, forming pressure 10Torr, RF power 100W, TEOS flow 50SCCM, oxygen ( $O_2$ ) flow 1SLM, 5% of an ozone level, the hydrogen peroxide ( $H_2O_2$ ) flow 0 - 5SCCM. Drawing 16 is the figure which compared the longitudinal plane shape on the aluminum wiring 245 of the insulator layer formed by various methods. The insulator layer (henceforth a TEOS/ $O_2$  system plasma-CVD film) and drawing 16 (b) which used the plasma vapor phase growth of the conventional TEOS and oxygen ( $O_2$ ) drawing 16 (a), When a hydrogen peroxide ( $H_2O_2$ ) flow is 0SCCM among the conditions of this example (when it was got blocked and only ozone content oxygen is used). Drawing 16 (c) shows the case where a hydrogen peroxide ( $H_2O_2$ ) flow is 5SCCM among the conditions of this example. Although drawing 16 (a) and (b) show that step coverage has been considerably improved by using ozone content oxygen instead of oxygen, in the space to which an aspect ratio exceeds 1.0, it also turns out that the void (\*\*) 249 arises. From drawing 16 (c), by adding hydrogen peroxide gas ( $H_2O_2$ ) further in addition to ozone content oxygen, Generating of a void (\*\*) is lost also in the space to which an aspect ratio exceeds 1.0, and it turns out that flow shape was formed a little also in the portion of isolated aluminum wiring. The added hydrogen peroxide decomposes according to a chemical formula like a formula (1), and these results are  $H_2O_2 \rightarrow H_2O + \cdot O \dots$  (1)

It is thought that it is because the film formation precursor pseudo-liquid layer 59 is formed also in the state where generation of the film formation precursor 50 shown by drawing 3 is promoted, high-frequency power is impressed, and plasma is irradiated in order that an oxygen radical ( $\cdot O$ ) and water ( $H_2O$ ) may be generated and these may promote the polymerization of TEOS.

[0053]Although hydrogen peroxide was used as addition gas in this example, The same result was obtained, although the effect had a difference when hydrogen ( $H_2$ ), water ( $H_2O$ ), hydrocarbon, alcohol, a carbonyl compound, and the compound that reacts to oxygen like carboxylic acid and generates water ( $H_2O$ ) were used.

Also when hydrogen peroxide was used and an RF output was zero, the improvement of flow nature was accepted compared with the case where hydrogen peroxide is not used. Although the ethyl silicate (TEOS: chemical formula  $Si(OC_2H_5)_4$ ) was used as organic silane gas in this example, A tetramethylsilane (TMS: chemical formula  $Si(CH_3)_4$ ), Tetramethyl cyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS), Hexamethyldisilazane (HMDS), triethoxysilane (chemical formula  $SiH(OC_2H_5)_3$ ), The same result is obtained even if it uses silicon containing compounds, such as a tris dimethylamino silane (chemical formula  $SiH(N(CH_3)_2)_3$ ).

[0054] Drawing 15 is outline drawing of longitudinal section of the plasma chemistry vapor phase growth system of the 7th example of this invention. In the device of this example, the ethyl silicate (it calls the following TEOS) gas used as a silicon raw material, Carry out flow regulation of the TEOS on a fluid supplied from the TEOS tank which is not expressed with this figure with the mass flow type liquid flow rate regulator 210, and it is made to evaporate thoroughly with the evaporator 222, and it is mixed with the nitrogen gas by which flow regulation was carried out by the flow regulator 211, and is generated. Ozone containing oxygen introduces into the silent discharge type ozone generator 221 the oxygen gas by which flow regulation was carried out by the flow regulator 209, makes 1 to 10% of ozone contain, and is generated. Hydrogen peroxide gas is generated by carrying out bubbling of the fluid hydrogen peroxide 220 in the homoiothermal container 219 with the helium by which flow regulation was carried out with the flow regulator 212. Although the concentration of hydrogen peroxide gas was adjusted at the temperature of the homoiothermal container 219, it was used in 10-20 \*\* at this example. Thus, the TEOS gas, ozone containing oxygen gas, and hydrogen peroxide gas which were generated are introduced into the manifold 244 from the TEOS feed port 224, the ozone feed port 223, and the hydrogen peroxide gas inlet 225. Within a manifold, it is mixed and these gases are diffused almost uniformly by hitting the gas diffusion board 227. If it hits the shower electrode 229, it will distribute still more uniformly and the surface of the substrate 243 will be sprayed. It is equipped on the SiC susceptor 231, optical heating is carried out from the heat lamp 233 through the quartz plate 232, and the substrate 243 is held at the temperature of about 200-450 \*\*. The exhaust pipe 234 is connected to the vacuum pump 236, and the pressure inside the reaction chamber 230 is held at 0.1 - tens Torr (s). The shower electrode 229 is electrically insulated with other portions with the insulating ring 228. The 13.56-MHz high frequency generated with RF oscillator 241 is impressed.

\*\*\*\* control of the output of this RF oscillator 241 is carried out at the pulse generated with the pulse generator 242.

Periodically or intensity changes.

[0055] The above devices are used in this example, The forming temperature of 350 \*\*, forming pressure 10Torr, RF frequency of 13.56 MHz, RF power 100W, the pulse frequency of 1 Hz, D= 30% of duty ratio, TEOS flow 50SCCM, oxygen ( $O_2$ ) flow 1SLM, 5% of an ozone level, hydrogen peroxide. ( $H_2O_2$ ) The insulator layer was formed by the film formation condition of the flow 0 - 5SCCM. Drawing 17 shows the longitudinal plane shape on the aluminum wiring 251 of the insulator layer formed by the film formation condition of this example. According to this example, a figure shows that it not only embeds the space part in which an aspect ratio exceeds 1.0, but flow shape is obtained and the insulator layer which has a smooth surface state is obtained.

[0056] In this example, although 13.56 MHz was used as frequency of a RF oscillator, if low frequency waves, such as 450 Hz, are added, a still better result will be obtained like Example 1 of this invention. In this example, although ON-OFF of RF power was performed using the pulse generator, even if it repeats the state where it does not glare [ an exposure and ] of plasma, the same result is obtained using a device like drawing 6. Although the ethyl silicate (TEOS: chemical formula  $Si(OC_2H_5)_4$ ) was used as organic silane gas in this example, A tetramethylsilane (TMS: chemical formula  $Si(CH_3)_4$ ), Tetramethyl cyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS), Hexamethyldisilazane (HMDS), triethoxysilane (chemical formula  $SiH(OC_2H_5)_3$ ), The same result is obtained even if it uses silicon containing compounds, such as a tris dimethylamino silane (chemical formula  $SiH(N(CH_3)_2)_3$ ).

[0057] Drawing 18 is outline drawing of longitudinal section of the plasma chemistry vapor phase growth system of the 8th example of this invention. Octamethylcyclotetrasiloxane which serves as a silicon raw material in the device of this example (it calls the following OMCTS.) A chemical formula is  $Si_4O_{12}C_8H_{24}$ . Gas, Carry out flow

regulation of the liquid OMCTS supplied from the OMCTS tank which is not expressed with this figure with the mass flow type liquid flow rate regulator 255, and it is made to evaporate thoroughly with the evaporator 265, and it is mixed with the nitrogen gas by which flow regulation was carried out by the flow regulator 256, and is generated. Ozone content oxygen introduces into the silent discharge type ozone generator 264 the oxygen gas by which flow regulation was carried out by the flow regulator 254, makes 0.1 to 1.0% of ozone contain, and is generated. Ammonia gas is supplied from  $\text{HN}_3$  gas bomb which is not expressed with this figure, and flow regulation is carried out by flow control term 257. Thus, the OMCTS gas, ozone containing oxygen gas, and ammonia gas which were generated are introduced into the manifold 269 from the OMCTS feed port 267, the ozone feed port 268, and the  $\text{NH}_3$  feed port 266. Within a manifold, it is mixed and these gases are diffused almost uniformly by hitting the gas diffusion board 271. If it hits the shower electrode 273, it will distribute still more uniformly and the surface of the substrate 275 will be sprayed. It is equipped on the SiC susceptor 276, optical heating is carried out from the heat lamp 278 through the quartz plate 277, and the substrate 275 is held at the temperature of about 200-450 \*\*. The exhaust pipe 279 is connected to the vacuum pump 281, and the pressure inside the reaction chamber 274 is held at 0.1 - the suitable value of tens Torr(s). The shower electrode 273 is electrically insulated with other portions with the insulating ring 272. The 13.56-MHz high frequency generated by the RF generator 286 is impressed. The output of this RF oscillator 286 is controlled by the pulse generated with the pulse generator 287. Periodically or intensity changes.

[0058]In this example, using the above devices, the forming temperature of 300 \*\*, forming pressure 1.0Torr, RF frequency of 13.56 MHz, RF power 300W, the pulse frequency of 0.2 Hz (pulse cycle 5 seconds), The insulator layer was formed by the film formation condition of D= 20% of duty ratio, OMCTS flow 50SCCM, oxygen ( $\text{O}_2$ ) flow 0.1SLM, 1% of an ozone level, and ammonia ( $\text{NH}_3$ ) flow 1.0SLM.

[0059]The film growth rate of about 1200 Å / min was obtained as a result, and step coverage was not less than 90%. The presentation is SiON whose nitrogen content is 5 to 25%. It turned out that a film Nakamizu daily dose is also an insulator layer good at 1% or less.

[0060]The membrane formation mechanism of the insulator layer of this example is explained as follows. First, the heat CVD reaction of ozone and OMCTS is performed in the state of OFF of RF power. The  $\text{SiO}_2$  film having contained quite many moisture is formed at this reaction. Next, if RF power is set to ON, ammonia plasma will occur. If the  $\text{SiO}_2$  film formed by the heat CVD reaction is put to this ammonia plasma, a nitrogen ion will be poured in and it will be considered nitriding. The plasma-CVD reaction has also produced the time of ON of RF power simultaneously.

Since Si, O, N, and H are contained in reactant gas, a SiON film is formed.

In this example, DEPORETO of the plasma-CVD reaction to which DEPORETO of the heat CVD reaction of ozone and OMCTS turned ON about 1000 Å / min, and RF power is 2000 Å / min, Since the time of RF power OFF is 4 seconds, it means putting the  $\text{SiO}_2$  film of about 125-Å thickness to ammonia plasma. The artificer of this invention is checking nitriding [ the  $\text{SiO}_2$  film of thickness of this level / ammonia plasma ] easily.

And it is also checking that composition distribution and membraneous distribution hardly arise in a thickness direction by ON-OFF of RF power.

[0061]In this example, although 13.56 MHz was used as frequency of a RF oscillator, if low frequency waves,

such as 450 Hz, are added, a still better result will be obtained like Example 1 of this invention. In this example, although ON-OFF of RF power was performed using the pulse generator, even if it repeats the state where it does not glare [ an exposure and ] of plasma, the same result is obtained using a device like drawing 6. Although octamethylcyclotetrasiloxane (OMCTS) was used as organic silane gas in this example, An ethyl silicate (TEOS:Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>), A tetramethylsilane (TMS:Si(CH<sub>3</sub>)<sub>3</sub>), The same result is obtained even if it uses silicon containing compounds, such as tetramethyl cyclotetrasiloxane (TMCTS), hexamethyldisilazane (HMDS), and triethoxysilane (SiH(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>). As organic silane gas, a tris dimethylamino silane (SiH(N(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), a tris diethylamino silane (SiH(N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>)<sub>3</sub>), etc., Nitrogen content can be raised if the compound which has Si-N combination is used. Although ammonia (NH<sub>3</sub>) was used in this example as gas made to generate the plasma which pours in nitrogen, the effect that the mixed gas of N<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub> is also the same is acquired.

[0062]Drawing 19 is drawing of longitudinal section showing the outline of the plasma chemistry vapor phase growth system of the 9th example of this invention.

[0063]Ammonia gas NH<sub>3</sub> by which flow regulation was carried out to the ion source cave 305 by the flow regulator 288, Nitrogen gas N<sub>2</sub> by which flow regulation was carried out to laughter gas N<sub>2</sub>O by which flow regulation was carried out by the flow regulator 289 by the flow regulator 290 is supplied, and the pressure is maintained at p=100mTorr. Microwave with a frequency of 2.45 GHz is supplied via the waveguide 299 and the transmission window 298 from the microwave power supply 300. By the 875 gauss magnetic field which the main electromagnet coil 303 makes, within the ion source cave 305, the electron cyclotron resonance (ECR) has happened and the high plasma of an ionization rate occurs. With the emission magnetic field and the auxiliary coil 1.304 of the main electromagnet 303, the oxygen ion, nitrogen ion, and hydrogen ion which are generated here are pulled out to the reaction chamber 309, pass through the crevice between the grids 307, and it is irradiated with them to the substrate 310. The grid 307 rebounds ion with the voltage to impress, or is carrying out the duty of the shutter which makes it pass.

[0064]The TDEAS gas used as a silicon raw material the TDEAS gas which evaporated from TDEAS(fluid)318 kept warm in the homoiothermal container 317 kept at 80 \*\*, Flow regulation is carried out by the flow regulator 292, and it is mixed with the nitrogen gas by which flow regulation was carried out by the flow regulator 291, and is introduced from the source gas feed port 308 to a reaction chamber, and a substrate face is sprayed. Here, piping and the source gas feed port 308 which are connected with the source gas feed port 308 from the homoiothermal container 317 containing TDEAS318 are maintained at the constant temperature of not less than 80 \*\*. It is equipped with the substrate 310 on the susceptor 312, and it is heated by 300 \*\* with the heater 315. The pressure of the reaction chamber is maintained at about 1 mTorr by the vacuum pump 316.

[0065]In the plasma CVD device of this example, first, the microwave power supply 300 is operated, an 875 gauss magnetic field is generated with a main electromagnet coil, ECR resonance is produced and the plasma which consists of nitrogen gas, ammonia gas, and laughter gas in the ion source cave 305 is generated. It is suitable, and it comes out, and is made the small value, and the exposure of plasma makes the current sent through the auxiliary coils 1 and 304 and the auxiliary coils 2 and 311 the grade which generates the magnetic field which faces to a substrate from an ion source and which becomes uniform. The ion electrified in positive [, such as oxygen ion O<sup>+</sup> / which impresses positive voltage to the grid 307 and exists in plasma /, nitrogen ion N<sup>+</sup>, and hydrogen ion H<sup>+</sup>, ] recoils by a positive electric field, and the substrate 310 is kept from being irradiated. In this state, only neutral active species (radical) and molecule which were generated in the plasma in the ion source cave 305 are supplied to the substrate 310 surface. Here, if TDEAS gas is supplied, the thermal reaction activated with neutral active species (radical) will occur, and a SiON film with sufficient step coverage will be



formed. In this example, about 10 nm of SiON films by this thermal reaction were formed. Next, voltage impressed to the grid 307 is made into zero or a negative small value, and it is made for the just electrified ion to be irradiated by the surface of the substrate 310. Then, by receiving an ion bombardment, the moisture and carbon in a film \*\*\*\* and the SiON film formed by thermal reaction turns into a plasma-CVD film and a good SiON film of membraneous quality which has equivalent membraneous quality. In a substrate face, the plasma chemical reaction has also occurred and plasma CVD and a SiON film are also formed simultaneously. Then, the number of ion which will be irradiated with it by the substrate 310 if the voltage impressed to the grid 307 is changed with the cycle of 1 to about 10 seconds will change periodically, and formation of heat CVD and the SiON film by thermal reaction and refining to plasma CVD and a SiON film will be performed by turns. As a result, plasma CVD and a SiON film excellent in step coverage and a level difference embedding positive are formed. Since the reaction chamber pressure is especially set to about 1 mTorr by this example, the embedding of the big slot on the aspect ratio is also possible.

[0066]Although the recoil electric field by impressing positive voltage to the grid 307 was used in the above-mentioned example as a means to change the ion irradiated by the substrate 310, The mirror type magnetic field by the auxiliary coils 1 and 304, the cusp type magnetic field formed with the auxiliary coils 2 and 311, and the recoil electric field formed in the susceptor 312 by impressing positive voltage from the bias application power supply 313 may be used. Although not shown in drawing 19, the same result is obtained even if it uses a mechanical shutter. However, when it is made structure which bars radical diffusion using a mechanical shutter etc., it cannot be overemphasized that it is better to supply a radical near the substrate using a radical generator, to promote thermochemistry vapor phase epitaxy, and to have promoted growth of the heat CVD film.

[0067]In the above-mentioned example, although the electron cyclotron resonance type (ECR) ion source was used as an ion source, if the intensity of ion can be changed, it will not be based on the form but the same result will be obtained.

[0068]Although the tris diethylamino silane (TDEAS: chemical formula  $\text{SiH}(\text{N}(\text{C}_2\text{H}_5)_2)_3$ ) was used as organic silane gas in this example, An ethyl silicate (TEOS: chemical formula  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ), A tetramethylsilane (TMS: chemical formula  $\text{Si}(\text{CH}_3)_4$ ), Tetramethyl cyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS), Hexamethyldisilazane (HMDS), triethoxysilane (chemical formula  $\text{SiH}(\text{OC}_2\text{H}_5)_3$ ), The same result is obtained even if it uses silicon containing compounds, such as a tris dimethylamino silane (chemical formula  $\text{SiH}(\text{N}(\text{CH}_3)_2)_3$ ).

[0069]The same result is obtained also when hydrides and organic compounds, such as nitrogen compounds, such as silicon inorganic compounds, ammonia, etc., such as Silang, Lynn, boron, arsenic, antimony, are made to mix into reactant gas. Although ammonia ( $\text{NH}_3$ ) was used as gas made to generate plasma in this example, the effect that the mixed gas of  $\text{N}_2$ ,  $\text{N}_2$ , and  $\text{H}_2$  is also the same is acquired.

[0070]

[Effect of the Invention]As explained above, the chemical-vapor-deposition method of this invention, The ozone which has the outstanding step coverage while changing the plasma irradiation intensity to a substrate face periodically, and formation of the heat CVD film of TEOS, In order to repeat refining to membraneous quality equivalent to the plasma-CVD film of the heat CVD film, and formation of plasma TEOS and a CVD film and to perform them, It has such excellent step coverage, and a film Nakamizu daily dose and the stress in a film are small, and it is effective in formation of the plasma-CVD film which has good membraneous quality being attained that it is detailed and it is possible to embed the large slot on the aspect ratio. Since the chemical-vapor-deposition method of this invention contains addition gas other than organic Silang and ozone, such as hydrogen

peroxide, as material gas, formation of the insulator layer which was excellent in embedding nature and flow nature is attained.

[0071]the mechanism in which the chemical vapor deposition apparatus of this invention supplies organic Silang, the mechanism which supplies oxygen or ozone content oxygen, and the mechanism to which plasma generation intensity is changed periodically -- or, several plasma irradiation mechanisms which differ in the plasma strength provided in one reaction vessel, and the mechanism to which a substrate is moved among two or more of these plasma irradiation mechanisms -- or, Since it has a mechanical or electromagnetic shutter for changing plasma irradiation intensity periodically, the plasma chemistry vapor phase growth of this invention is effectively realizable. The chemical vapor deposition apparatus of this invention has hydrogen peroxide, hydrogen, water, hydrocarbon, alcohol, a carbonyl compound, and a mechanism that makes a gaseous state at least one kind in carboxylic acid, and supplies it.

The chemical-vapor-deposition method of this invention is effectively realizable.

[0072]. [ whether the chemical-vapor-deposition method given in this invention for which addition gas, such as organic Silang, oxygen, or ozone, hydrogen peroxide, is used as a raw material is used for the manufacturing method of the multilevel interconnection of this invention, and ] . Or make organic Silang, oxygen, or ozone into material gas, and change the plasma irradiation intensity to a substrate face periodically. Since the process at which only the thickness more than the height of metallic wiring forms an insulator layer without generating of \*\* (void) between metallic wiring is included using plasma chemistry vapor phase growth given in this invention, Compared with the manufacturing method of the conventional multilevel interconnection using a silica coating film, the moisture content in an interlayer film decreases substantially, and improvement in crack resistant improvement, low-pass [ of a stress migration ], and the flow characteristic of a through hole, etc. are achieved. Since the routing counter of the manufacturing method of the multilevel interconnection of this invention is decreasing remarkably compared with the conventional method, its yield improves and it is effective in cost being reduced.

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[Translation done.]

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TECHNICAL FIELD

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[Industrial Application]This invention relates to the manufacturing method of a chemical-vapor-deposition method,  
a chemical vapor deposition apparatus, and multilevel interconnection.

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[Translation done.]

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PRIOR ART

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[Description of the Prior Art]The conventional plasma chemistry vapor phase growth formed the desired thin film on the processed board, using TEOS and oxygen for reactant gas, impressing the high-frequency power of a fixed output between the counterelectrodes in a reaction vessel, and generating the plasma of constant intensity.

[0003]The schematic diagram of the conventional plasma vapor phase growth system is shown in drawing 9.

[0004]The TEOS (tetraethyl orthosilicate) gas used as a silicon raw material carries out bubbling of the liquid TEOS131 put into the bubbler 132 by helium (helium) gas by which flow regulation was carried out by the flow regulator 123, evaporates TEOS, and is generated. Ozone content oxygen passes the ozone generator 165 for the oxygen gas by which flow regulation was carried out by the flow regulator 120, makes ozone of about 10% of concentration contain, and is generated. TEOS gas and ozone containing oxygen gas are introduced into the manifold 136 from the TEOS feed port 138, and oxygen and an ozone feed port 139, It is mixed within the manifold 136, and it hits the gas diffusion board 140, is spread, and distributes still more uniformly through the shower electrode 142, and the surface of the substrate 147 is sprayed. It is equipped on the SiC susceptor 144, optical heating is carried out from the heat lamp 146 through the quartz plate 145, and the substrate 147 is held at the temperature of about 350 \*\*. The shower electrode 142 is electrically insulated with other portions with the insulating ring 141.

The high frequency voltage of two frequency generated with 13.56-MHz RF generator 129 and the high-pass filter 130, 450-kHz RF generator 133, and the low pass filter 134 is impressed via the matching box 135.

The exhaust pipe 148 is connected to the vacuum pump 149, and the pressure of the reaction chamber 143 is held at the number Torr.

[0005]Usually, in the above devices, after spraying TEOS gas and the mixed gas of oxygen on the substrate 147 from the shower electrode 142 and checking the stability of a pressure etc. first, impress fixed high frequency voltage to the shower electrode 142, TEOS and oxygen are made to decompose, and a desired film is formed on the substrate 147.

[0006]In such a simple method, it turns out that the step coverage nature (step coverage) to the ground stepped surface of the formed film is bad (about 50%), and to perform plasma chemistry vapor phase growth, and ozone and the thermochemistry vapor phase growth of TEOS by turns is tried. When performing such a method to drawing 10, the change to the membrane formation time of the high-frequency power impressed to the shower electrode 142, the number of oxygen ion in plasma, and the ozone level in material gas is shown. Plasma chemistry vapor phase epitaxy is performed, and the period when high-frequency power is impressed is performing ozone thermochemistry vapor phase epitaxy, although the number of oxygen ion shows the maximum. As for the period of zero, also in the number of oxygen ion, high-frequency power is zero.

After making high-frequency power into zero, in order to begin to pass ozone, fixed time is required by the time an ozone level rises. As mentioned above, when plasma chemistry vapor phase growth and ozone thermochemistry

vapor phase growth are performed by turns, it is shown in drawing 11 (a) - (d) how a film is formed. On the aluminum wiring 153 formed on the substratum substrate, first, as shown in (b), the plasma CVD film 154 is formed. Next, as shown in (c), in order to embed the narrow space between aluminum wiring, 1st heat CVD film 155 is formed. As shown in (d), the 2nd plasma-CVD film 156 is formed. Such a process is repeated, film formation is performed to desired thickness, and the film of multilayer structure is formed like drawing 11 (d). It is important that ozone heat CVD film 155 remains in the form as it is by such a method especially. Because, if the film formation condition of ozone heat CVD film 155 is not proper, many moisture remains in a film, The problem that a steam blows off from the interlayer connection hole of aluminum wiring, exfoliation of an interlayer film arises with a steam, or the faulty connection (a poor through hole) in the interlayer connection hole of aluminum wiring occurs arises. It is known to these problems that it is effective to form ozone heat CVD film 155 on high ozone level conditions. However, under such high ozone level conditions, it is also known that the step coverage of ozone heat CVD film 155 on the 1st plasma-CVD film 154 will deteriorate. This is considered that the membranous quality of the 1st plasma-CVD film 154 happens since it differs on the upper surface and the side of the aluminum wiring 153.

[0007]Drawing 12 shows the formation method of the flattening insulator layer for multilevel interconnection which used conventional plasma chemistry vapor phase growth and the silica applying method. First, as shown in drawing 12 (a) and (b), only the thickness which is a grade where \*\* (void) is not made to the space between wiring forms the plasma-CVD film 159 on the aluminum wiring 158 formed on the substrate 157. Next, silica coating liquid is applied like drawing 12 (c), heat treatment of around 300 \*\* for 100 \*\* heat treatment for solvent evaporation and a membranous improvement is performed, and the silica coating film (1-time spreading) 160 is formed. The way things stand, since surface smoothness is insufficient, the process of silica spreading and heat treatment which were performed by drawing 12 (c) is repeated twice or more like drawing 12 (d), and the silica coating film (multiple-times spreading) 161 is formed. Etchback is carried out using the usual reactive-ion-etching method (RIE). Since an oxygen atom will be supplied from an oxide film if the plasma-CVD oxide film on aluminum wiring is exposed at this time, The etching rate of a silica coating film becomes large, and, as for the silica coating film 162 behind etchback, cratering the space part between aluminum wiring level differences is known like drawing 12 (e). Finally, again, the plasma-CVD film 163 is formed and an interlayer film is completed.

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[Translation done.]

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**EFFECT OF THE INVENTION**

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[Effect of the Invention]As explained above, the chemical-vapor-deposition method of this invention, The ozone which has the outstanding step coverage while changing the plasma irradiation intensity to a substrate face periodically, and formation of the heat CVD film of TEOS, In order to repeat refining to membraneous quality equivalent to the plasma-CVD film of the heat CVD film, and formation of plasma TEOS and a CVD film and to perform them, It has such excellent step coverage, and a film Nakamizu daily dose and the stress in a film are small, and it is effective in formation of the plasma-CVD film which has good membraneous quality being attained that it is detailed and it is possible to embed the large slot on the aspect ratio. Since the chemical-vapor-deposition method of this invention contains addition gas other than organic Silang and ozone, such as hydrogen peroxide, as material gas, formation of the insulator layer which was excellent in embedding nature and flow nature is attained.

[0071]the mechanism in which the chemical vapor deposition apparatus of this invention supplies organic Silang, the mechanism which supplies oxygen or ozone content oxygen, and the mechanism to which plasma generation intensity is changed periodically -- or, several plasma irradiation mechanisms which differ in the plasma strength provided in one reaction vessel, and the mechanism to which a substrate is moved among two or more of these plasma irradiation mechanisms -- or, Since it has a mechanical or electromagnetic shutter for changing plasma irradiation intensity periodically, the plasma chemistry vapor phase growth of this invention is effectively realizable. The chemical vapor deposition apparatus of this invention has hydrogen peroxide, hydrogen, water, hydrocarbon, alcohol, a carbonyl compound, and a mechanism that makes a gaseous state at least one kind in carboxylic acid, and supplies it.

The chemical-vapor-deposition method of this invention is effectively realizable.

[0072]. [ whether the chemical-vapor-deposition method given in this invention for which addition gas, such as organic Silang, oxygen, or ozone, hydrogen peroxide, is used as a raw material is used for the manufacturing method of the multilevel interconnection of this invention, and ] . Or make organic Silang, oxygen, or ozone into material gas, and change the plasma irradiation intensity to a substrate face periodically. Since the process at which only the thickness more than the height of metallic wiring forms an insulator layer without generating of \*\* (void) between metallic wiring is included using plasma chemistry vapor phase growth given in this invention, Compared with the manufacturing method of the conventional multilevel interconnection using a silica coating film, the moisture content in an interlayer film decreases substantially, and improvement in crack resistant improvement, low-pass [ of a stress migration ], and the flow characteristic of a through hole, etc. are achieved. Since the routing counter of the manufacturing method of the multilevel interconnection of this invention is decreasing remarkably compared with the conventional method, its yield improves and it is effective in cost being reduced.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention]The above-mentioned conventional plasma chemistry vapor phase growth had bad step coverage nature (step coverage), and was not able to lay the submicron space between aluminum wiring underground. In order to lay the submicron space between aluminum wiring underground, it is necessary to perform plasma chemistry vapor phase growth, and ozone and the thermochemistry vapor phase growth of TEOS by turns, or to form a silica coating film like drawing 12 like drawing 11, many times. However, the ozone TEOS heat CVD film formed under decompression of about 10 Torr and the silica coating film had much moisture contained in a film, there was a problem in opportunity intensity, an insulating property, etc., and there was a fault that the faulty connection of the through hole which connects lower layer aluminum wiring and the upper aluminum wiring especially arose. When membranes were formed on high ozone level conditions, the amount of film Nakamizu decreased, but step coverage deteriorated and there was fault where perfect embedding becomes impossible. In the method of carrying out etchback of a silica coating film like drawing 12 further again, the process of forming a silica coating film, and the process which carries out etchback were dramatically complicated, and the increase in a routing counter and the fault of causing yield lowering also had it.

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MEANS

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[Means for Solving the Problem]A chemical-vapor-deposition method of this invention contains organic Silang, and oxygen or ozone as material gas, Furthermore, at least one kind in hydrogen peroxide ( $H_2O_2$ ), hydrogen ( $H_2$ ), water ( $H_2O$ ), hydrocarbon, alcohol, a carbonyl compound, and carboxylic acid is included. Plasma chemistry vapor phase growth of this invention forms a desired film, changing plasma irradiation intensity to a substrate face periodically including organic Silang, oxygen, or ozone content oxygen to at least a part of material gas. Under the present circumstances, repeat and perform a generation state and a non-generation state of plasma as a means to change plasma irradiation intensity, or. It repeats an exposure of plasma to a substrate face, and un-glaring, or high frequency voltage of two or more sorts of frequency is impressed to an electrode in a reaction vessel which counters, and high-frequency power of some or all of them is changed periodically.

[0010]A chemical vapor deposition apparatus of this invention is provided with the following.

A mechanism which supplies organic Silang.

A mechanism which supplies ozone content oxygen.

Hydrogen peroxide, hydrogen, water, hydrocarbon, alcohol, a carbonyl compound, a mechanism that makes a gaseous state at least one kind in carboxylic acid, and supplies it.

A chemical vapor deposition apparatus of this invention is provided with the following.

A mechanism which supplies organic Silang.

A mechanism which supplies oxygen or ozone content oxygen.

A mechanism to which plasma generation intensity is changed periodically, or several plasma irradiation mechanisms from which plasma strength provided in one reaction vessel differs.

A mechanism to which a substrate is moved among two or more of these plasma irradiation mechanisms.

A chemical vapor deposition apparatus of this invention is provided with the following.

A mechanism which supplies organic Silang and ozone content oxygen to a wafer surface.

Oxygen plasma ion sources.

A mechanical or electromagnetic shutter for changing plasma irradiation intensity periodically.

A chemical vapor deposition apparatus of this invention impresses high frequency voltage of two or more sorts of frequency to an electrode in a reaction vessel which counters, and has a mechanism to which high-frequency power of some or all of them is changed periodically.

[0011]A manufacturing method of multilevel interconnection of this invention to material gas Organic Silang, Including ozone or oxygen, further by a chemical-vapor-deposition method of hydrogen peroxide, hydrogen, water, hydrocarbon, alcohol, a carbonyl compound, and the carboxylic acid which adds one at least. A process at which only thickness more than height of metallic wiring forms an insulator layer on metallic wiring, a process of forming flattening films, such as a resist film and organic silica membrane, and a process which carries out etchback by a reactive-ion-etching method are included. A process at which a manufacturing method of multilevel

interconnection of this invention makes organic Silang, ozone, or oxygen material gas, plasma irradiation intensity to a substrate face is changed periodically, and only thickness more than height of metallic wiring forms an insulator layer on metallic wiring, A process of forming flattening films, such as a resist film and organic silica membrane, and a process which carries out etchback by a reactive-ion-etching method are included.

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EXAMPLE

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[Example]Next, this invention is explained with reference to drawings.

[0013]Drawing 1 is outline drawing of longitudinal section of the plasma chemistry vapor phase growth system showing the 1st example of this invention.

Drawing 2 expresses operation of a plasma chemistry vapor-phase-epitaxy difference of drawing 1 about the temporal change of impression high-frequency power, the number of oxygen ion, and an ozone level, and drawing 3, Are the outline of the principle of this invention a model figure which expresses, and drawing 4, the time of being drawing of longitudinal section showing the growth process of the time progress and the film at the time of performing operation like drawing 2, and drawing 5 performing operation like drawing 2 -- high frequency ON time ( $t_{ON}$ ) -- the relation of a film growth rate, step coverage, and the absorption index of an OH radical is shown comparatively (duty D).

[0014]Drawing 1 is outline drawing of longitudinal section of the plasma chemistry vapor phase growth system of Example 1 of this invention. In the device of this example, the ethyl silicate (it calls the following TEOS) gas used as a silicon raw material, Carry out flow regulation of the liquid TEOS supplied from the TEOS tank which is not expressed with this figure with the mass flow type liquid flow rate regulator 3, and it is made to evaporate thoroughly by evaporation term 12, and it is mixed with the helium by which flow regulation was carried out by the flow regulator 4, and is generated. Ozone content oxygen introduces into the silent discharge type ozone generator 11 the oxygen by which flow regulation was carried out by the flow regulator 2, makes 1 to 10% of ozone contain, and is generated. Thus, the TEOS gas and ozone containing oxygen gas which were generated are introduced into the manifold 15 from the TEOS feed port 14 and the ozone feed port 13. Within a manifold, it is mixed and these gases are diffused almost uniformly by hitting the gas diffusion board 17. If it hits the shower electrode 19, it will distribute still more uniformly and the surface of the substrate 28 will be sprayed. It is equipped on the SiC susceptor 21, optical heating is carried out from the heat lamp 23 through the quartz plate 22, and the substrate 28 is held at the temperature of about 200-450 \*\*. The shower electrode 19 is electrically insulated with other portions with the insulating ring 18.

The high frequency voltage of two frequency generated with the source 36 and the low pass filter 35 is impressed via the matching box 37 by 13.56-MHz RF generator 39 and the high-pass filter 38, and 450-kHz high frequency. The exhaust pipe 24 is connected to the vacuum pump 26, and the pressure of the reaction chamber 20 is held at 0.1 - tens Torr(s).

[0015]The mixer part which mixes the high frequency voltage of two frequency inside the matching box 37 connected to the shower electrode 19 in this example, There are a matching part which performs an impedance match, a dummy load, and a solid state switch, and the high frequency voltage impressed to the shower electrode 19 can be turned now on and off. It is also possible to change the output of RF generators 35 and 36 and to

change the high frequency voltage impressed to the shower electrode 19 synchronizing with PASURU which the pulse generator 40 generates. These operations are controlled by the process controller 41 including substrate temperature, a reaction chamber pressure, etc. Transfer ways, such as these control signals, pulses, etc., are shown by the dashed line in drawing 1.

[0016]Here, operation of this device at the time of turning on and off the high frequency voltage impressed to the shower electrode 19 in periodic 1 second is explained using drawing 2, drawing 3, drawing 4, and drawing 5.

[0017]The drawing 2 \*\*\*\*\* shows the relation between membrane formation time and high-frequency power.

Plasma occurs between the shower electrode 19, the substrate 28, or the SiC susceptor 21 between time  $t_{ON}$  from which high-frequency power is turned on, and oxygen or ozone decomposes and it is generated by oxygen ion. The drawing 2 middle expresses change of the number of oxygen ion. Since it begins to impress high-frequency power, by the time the plasma state is stabilized, a certain fixed time will be required and will have become a waveform with sloping shoulders. Since ozone is more unstable than oxygen, the ionization efficiency by impression of high-frequency power is high. Therefore, like the drawing 2 upper row, the number of ozone molecules in plasma falls considerably, when high-frequency power is one.

[0018]Drawing 3 (a) and (b) is a model figure showing the situation near [ at the time of high frequency one and OFF ] the substrate face, respectively. Plasma occurs between the shower electrode 19 of drawing 1, and the substrate 28 at the time of high frequency ion. In plasma, an oxygen molecule and a TEOS molecule dissociate in the electron 45, the oxygen ion 47, the TEOS dissociation molecule 46, and oxygen radical 55 grade. Sheath voltage occurs between plasma and a substrate, it is accelerated with this voltage, and the drift of the oxygen ion 47 is carried out, and it collides with a substrate face. The TEOS dissociation molecule 46 is also diffused toward a substrate face, and it becomes the film formation precursor 50 by a pyrolysis or decomposition by an oxygen ion shock in a formation membrane surface. It reacts to an oxygen radical etc. in a formation membrane surface, and the formation film 51 is formed. Under the present circumstances, since very many oxygen ion shocks are shown in the surface of the formation film 51, the life of the film formation precursor 50 is quite short, and the density in a formation membrane surface is low. An oxygen ion shock has the operation which stiffens the formation film 51, and membraneous quality is good and is useful for formation of the film of compression stress.

[0019]Now, once high frequency is come by off (refer to drawing 3 (b)), an electron and the number of oxygen ion will decrease promptly, but the TEOS dissociation molecule 46 and the oxygen radical 55 remain still more. These are diffused on the surface of the formation film 51, serve as the film formation precursor 50, and decrease soon. It is spread toward a membrane surface, and the TEOS molecule 54 and the ozone molecule 56 also react, and serve as a TEOS dissociation molecule and a film formation precursor. In the surface of the formation film 51, since a film formation reaction is only thermal reaction, a film formation precursor exists in a formation membrane surface by high density, and the film formation precursor pseudo-liquid layer 59 is formed in it. The thickness of the side lower part of the level difference currently formed in the substrate 52 becomes thick, and this film formation precursor pseudo-liquid layer 59 eases inclination on the level difference side in order to show the character of a fluid.

[0020]Drawing 4 is drawing of longitudinal section showing time progress when high-frequency power is impressed like drawing 2, and the situation of film formation in model. First, like drawing 4 (a), high frequency is turned on between time  $t_{ON}$  (drawing 2 0.5 second), and 1st about 10-nm plasma-CVD film 60 is formed. Next, 1st heat CVD film 62 is formed between time  $t_{OFF}$  (0.5 second) like drawing 4 (b). Time  $t_{OFF}$  is dramatically as short as 0.5 second, and the thickness of 1st heat CVD film 62 is about 1 nm. Therefore, refining will be carried out with an oxygen ion shock etc. in early stages of the next  $t_{ON}$ , and it will be membraneous quality equivalent to a plasma-CVD film. Therefore, like drawing 4 (c), the 1st plasma-CVD film 60 and distinction stop attaching 1st

heat CVD film 62 by which refining was carried out, and it will be incorporated into the 1st plasma-CVD film 60. Since a heat CVD film is an effect of a film formation precursor pseudo-liquid layer, the angle of the narrow space between wiring or the level difference lower part can be embedded and shape can be made smooth, It means forming the formation film 64 before the 2nd plasma-CVD film growth of membraneous quality equivalent to plasma CVD in shape equivalent to the heat CVD by the continuing plasma irradiation in early stages of plasma-CVD film growth. Since the level difference lower part has roundish shape with the formation film 64 before the 2nd plasma-CVD film growth, the shape of the 2nd plasma-CVD film 63 formed on this is also roundish like drawing 4 (c). In order that distinction may not attach the formation film 64 before the 2nd plasma-CVD film growth, and the 2nd plasma-CVD film 63, either, in the growth step (d) of 2nd continuing heat CVD film 65, a lower layer film turns into the formation film 66 after the 2nd plasma-CVD film growth.

[0021]By repeating the above stages many times, like drawing 4 (e), there is no \*\* (void) in the space part between the aluminum wiring 61, and the formation film of good membraneous quality almost equivalent to a plasma-CVD film can be embedded.

[0022]Drawing 5 shows the relation between the value of duty ratio  $D (D = t_{ON} / (t_{ON} + t_{OFF}) \times 100 (\%))$  calculated from  $t_{ON}$  and  $t_{OFF}$  in drawing 2, and the absorption index of the OH radical in a growth rate, step coverage, and a film. The drawing 5 bottom shows that a growth rate increases, so that D is large, and it turns out that step coverage will begin to get worse if D exceeds 50%, and discontinuation shows becoming small enough, if, as for an OH radical, D exceeds 40% from the upper row. Although step coverage and a film Nakamizu daily dose (OH radical absorption index in a film) tend to conflict from drawing 4, by setting a duty ratio D value as the suitable range (it is 40 to 60% in the case of this example) shows that both can be prevented from spoiling.

[0023]Although the ethyl silicate (TEOS: chemical formula  $Si(OC_2H_5)_4$ ) was used as organic silane gas in this example, A tetramethylsilane (TMS: chemical formula  $Si(CH_3)_4$ ), Tetramethyl cyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS), The same result is obtained even if it uses silicon containing compounds, such as hexamethyldisilazane (HMDS), triethoxysilane ( $SiH(OC_2H_5)_3$ ), and a tris dimethylamino silane ( $SiH(N(CH_3)_2)_3$ ).

[0024]Since the life of an oxygen radical or a TEOS dissociation molecule is quite long even if ozone in reactant gas does not exist, the same result will be obtained if the value of duty ratio is chosen suitably. The same result is obtained also when hydrides and organic compounds, such as nitrogen compounds, such as silicon inorganic compounds, ammonia, etc., such as Silang, Lynn, boron, arsenic, antimony, are made to mix into reactant gas.

[0025]Although only the high-frequency power impressed to the shower electrode 19 was changed by this example further again, if high-frequency power, a reaction chamber pressure, substrate temperature, a gas mass flow, etc. are changed synchronizing with the pulse which the pulse generator 40 generates, better step coverage nature will be obtained.

[0026]Drawing 6 (a) is an outline top view of the reaction chamber of the plasma chemistry vapor phase growth system of the 2nd example of this invention.

Drawing 6 (b) is drawing of longitudinal section which met the A-A' line of drawing 6 (a).

Drawing 6 (a) expresses the top view which met the B-B' line of drawing 6 (b).

[0027]The reaction chamber 72 is divided into the field of six fanning, and fanning of the direction of 3:00 of a clock has become the heat CVD field 70.

Clockwise, it is arranged a plasma-CVD field, a heat CVD field, the plasma-CVD field 166, and by turns.

It is equipped with the substrate 69 on the susceptor 71 which rotates the axis of rotation 79 as an axis, and it passes through a heat CVD field and a plasma-CVD field by turns.

[0028]After TEOS gas and ozone content oxygen are introduced into the heat CVD field 70 and it distributes

uniformly with the gas distribution plate 83 and the shower injector 81 from the TEOS feed port 73 and the ozone feed port 75, the surface of the substrate 69 is supplied to it. Since the substrate 69 is heated by about 350 °C with the heater 80 installed in the back side of the susceptor 71, the heat CVD film by ozone and TEOS grows on a substrate.

[0029]TEOS gas and oxygen gas are introduced into the plasma-CVD field 166 from the TEOS feed port 73 and the oxygen feed port 74, it is uniformly distributed by gas distribution plate 83' and the shower electrode 78, and the surface of substrate 69' is supplied. The shower electrode 78 is electrically insulated from other portions of the reaction chamber by the insulating ring 82 and the insulator 76.

The high frequency voltage of 13.56 MHz or 450 kHz is impressed from RF introduction terminal 77.

Between the shower electrode 78, substrate 69', or the susceptor 71, plasma is excited by impression of such high frequency voltage, and a plasma-CVD film is formed.

[0030]As mentioned above, in order that the substrate 69 may pass through a plasma-CVD field and a heat CVD field by turns with the rotating susceptor 71, a plasma-CVD film and a heat CVD film are formed by turns. Under the present circumstances, if revolving speed of the susceptor 71 is made into a per minute 10 rotation grade, the thickness of the heat CVD film formed in the heat CVD field 70 is set to about 2 nm, plasma irradiation will be carried out in early stages of membrane formation of a plasma-CVD field, and membraneous quality will become being the same as that of a plasma-CVD film. Thus, as drawing 4 described, membraneous quality is the same as that of a plasma-CVD film, and the CVD film excellent in step coverage and level difference embedding nature is formed.

[0031]Although the reaction chamber was divided into six fields, this example will be available for it without limit, if this is two or more. Although the kind of film forming zone was made into two kinds, a heat CVD field and a plasma-CVD field, two or more sorts may be provided with the frequency and applied power of high frequency which impress a plasma-CVD field.

[0032]Although the susceptor 71 was made into the shape of a plane turntable and the shower injector and the shower electrode were provided up in this example, a susceptor is made into a cylinder or the shape of a multiple pillar, the lateral surface is equipped with a substrate, and the same result is obtained, even if it counters with a substrate and provides a shower electrode etc.

[0033]Although the ethyl silicate (TEOS: chemical formula  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) was used as organic silane gas in this example, A tetramethylsilane (TMS: chemical formula  $\text{Si}(\text{CH}_3)_4$ ), Tetramethyl cyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS), Hexamethyldisilazane (HMDS), triethoxysilane (chemical formula  $\text{SiH}(\text{OC}_2\text{H}_5)_3$ ). The same result is obtained even if it uses silicon containing compounds, such as a tris dimethylamino silane (chemical formula  $\text{SiH}(\text{N}(\text{CH}_3)_2)_3$ ).

[0034]Since the life of an oxygen radical or a TEOS dissociation molecule is quite long even if ozone does not exist in reactant gas, the same result will be obtained if the value of duty ratio is chosen suitably. The same result is obtained also when hydrides and organic compounds, such as nitrogen compounds, such as silicon inorganic compounds, ammonia, etc., such as Silang, Lynn, boron, arsenic, antimony, are made to mix into reactant gas.

[0035]Drawing 7 is a gross section figure showing the outline of the plasma chemistry vapor phase growth system of the 3rd example of this invention.

[0036]The argon gas Ar by which flow regulation was carried out to oxygen gas  $\text{O}_2$  by which flow regulation was carried out to the ion source cave 93 by the flow regulator 103 by the flow regulator 87 is supplied, and the pressure is maintained at  $p=1\text{mTorr}$ . Microwave with a frequency of 2.54 GHz is supplied via the waveguide 85 and the transmission window 86 from the microwave power supply 84. By the 875 gauss magnetic field which the main electromagnet coil 94 makes, within the ion source cave 93, the electron cyclotron resonance (ECR) has

happened and the high oxygen plasma of an ionization rate occurs. With the emission magnetic field and the auxiliary coil 96 of the main electromagnet coil 94, oxygen ion is pulled out to the reaction chamber 95, and it is irradiated with it to the substrate 106. The TEOS gas used as a silicon raw material carries out flow regulation of the TEOS gas which evaporated from TEOS111 kept warm in the homoiothermal container 112 kept at 80 °C by the flow regulator 113, and is introduced from the TEOS feed port 107 to a reaction chamber. The oxygen gas by which flow regulation was carried out with the flow regulator 101 passes the ozone generator 98, becomes ozone content oxygen, and is supplied from the ozone feed port 97. It is equipped with the substrate 106 on the susceptor 109, and it is heated by 300 °C with the heater 110. Flow regulation of the pressure of a reaction chamber is carried out by the flow regulator 88, and it is maintained at about 1 mTorr by the argon gas for dilution and the vacuum pump 105 which are supplied from the Ar feed port 108.

[0037]In the plasma CVD device of this example, oxygen plasma is first generated in the ion source cave 93. It is suitable, and it comes out, and is made the small value, and the exposure of oxygen plasma makes the auxiliary coil 96 and the current sent through 96' the grade which generates the magnetic field which faces to a substrate from an ion source and which becomes uniform. The magnetic field which faces to a substrate is generated, and it is suitable, and comes out from an ion source, and the current sent through reflective magnetic coil 102, 102' is also made into the small value. If the substrate 106 surface is made to irradiate with oxygen ion and TEOS gas is supplied in this state, ECR plasma vapor phase epitaxy will happen and the good plasma-CVD film of membraneous quality will be formed. About 10 nm is formed. Next, the value of the current sent through the auxiliary coil 96 and 96' is strengthened, a mirror type magnetic field is formed near an ion source cavernous exit, and it is made for the electron and ion which flow out of plasma by the main electromagnet coil 94 and the emission magnetic field of 94' to rebound. Then, on the substrate 106, only neutral particles diffused from TEOS gas and an ion source, such as an oxygen radical and an oxygen molecule, are supplied, only a heat CVD reaction occurs, and good membrane formation of step coverage is performed. Then, if the auxiliary coil 96 and the current sent through 96' are changed with the cycle of 1 to about 10 seconds, The number of oxygen ion irradiated by the substrate 106 changes periodically, a plasma-CVD film and a heat CVD film are formed by turns, further, refining to the plasma-CVD film of a heat CVD film is also performed, and the plasma CVD excellent in step coverage and level difference embedding nature is formed like drawing 4. Since the reaction chamber pressure is especially set to about 1 mTorr by this example, a winning popularity lump of the big slot on the aspect ratio also becomes possible.

[0038]Although the mirror type magnetic field formed with the auxiliary coil 94 was used in the above-mentioned example as a means to change the oxygen ion irradiated by the substrate 106, The cusp type magnetic field formed of reflective magnet 102, 102' and the recoil electric field formed in the susceptor 109 by impressing positive voltage may be used. Although not shown in drawing 7, the same result is obtained even if it uses an opportunity shutter. However, when it is made structure which bars diffusion of an oxygen radical using a mechanical shutter etc., it cannot be overemphasized that it is better to operate the ozone generator 98, to supply ozone near the substrate, to promote thermochemistry vapor phase epitaxy, and to have promoted growth of the heat CVD film.

[0039]In the above-mentioned example, although the electron cyclotron resonance type (ECR) ion source was used as an ion source, if the intensity of oxygen ion can be changed, it will not be based on the form but the same result will be obtained.

[0040]Although the ethyl silicate (TEOS: chemical formula  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) was used as organic silane gas in this example, A tetramethylsilane (TMS: chemical formula  $\text{Si}(\text{CH}_3)_4$ ), Tetramethyl cyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS), Hexamethyldisilazane (HMDS), triethoxysilane (chemical formula  $\text{SiH}(\text{OC}_2\text{H}_5)_3$ ), The same result is obtained even if it uses silicon containing compounds, such as a tris

dimethylamino silane (chemical formula  $\text{SiH}(\text{N}(\text{CH}_3)_2)_3$ ).

[0041]The same result is obtained also when hydrides and organic compounds, such as nitrogen compounds, such as silicon inorganic compounds, ammonia, etc., such as Silang, Lynn, boron, arsenic, antimony, are made to mix into reactant gas.

[0042]Drawing 8 is drawing of longitudinal section showing the interlayer insulation film flattening method of the 4th aluminum multilevel interconnection of this invention.

[0043]In this example, the aluminum wiring 114 is first formed on the substrate 115 in which the semiconductor device etc. were formed (drawing 8 (a)). Next, using the plasma chemistry vapor phase growth system of Example 1 of this invention, among a figure, as shown in (b) and (c), CVD film 116 of this invention is formed more thickly than the thickness of aluminum wiring. Postbake of the resist 117 is applied and carried out. Etchback is performed and it is made for the surface of a CVD film to become flat using the reactive-ion-etching method adjusted so that the etching rate of CVD film 116 of the resist 117 and this invention might become equal. Then, the interlayer film 118 by which flattening was carried out is done.

[0044]In this example, although resist was used for flattening, even if it uses polyethylene, organic SOG, etc., an equivalent result is obtained. As a flattening method, if grinding method is used, it will cross to an entire substrate and good surface smoothness will be obtained.

[0045]Drawing 13 shows the method of the operation of the 5th example which uses the plasma chemistry vapor phase growth system of Example 1 of drawing 1. It expresses with drawing 13 about 13.56-MHz high-frequency power, 450-kHz high-frequency power, ion current density, and average ion energy. However, any value is standardized at the maximum of each value.

[0046]In the method of operation of this example, like the 1st step and the 2nd step from under drawing 13, As a pulse is sent to RF generators 39 and 36 of two frequency (13.56 MHz and 450 kHz) of drawing 1 from the pulse generator 40 and the maximum output of the high frequency of two frequency becomes an opposite phase to them, voltage is impressed to the shower electrode 19. Then, like the 3rd step and the 4th step from under drawing 13, although change of ion current density is small, average ion energy takes the maximum, when 450-kHz high-frequency power is the maximum, and when 13.56-MHz high-frequency power is the maximum, it can serve as the minimum. If this has the high frequency of the high frequency to impress, it will be because the voltage (sheath voltage) produced between plasma and a substrate decreases. Thus, in that the intensity of an ion bombardment changes periodically, and does not have degradation of membraneous quality, and step coverage nature and slot embedding nature are improved, when changing only ion energy, although it is the same as that of Example 1, without changing ion current density, Like the drawing 13 highest rung, there is an advantage that change of a film growth rate can be small performed to about 10%.

[0047]In this example, although the device of drawing 1 was used, even if it uses the device of drawing 6 and drawing 7 which were shown in other examples of this invention, the same result can be obtained.

[0048]Although the ethyl silicate (TEOS: chemical formula  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) was used as organic silane gas in this example, A tetramethylsilane (TMS: chemical formula  $\text{Si}(\text{CH}_3)_4$ ), Tetramethyl cyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS), Hexamethyldisilazane (HMDS), triethoxysilane (chemical formula  $\text{SiH}(\text{OC}_2\text{H}_5)_3$ ), The same result is obtained even if it uses silicon containing compounds, such as a tris dimethylamino silane (chemical formula  $\text{SiH}(\text{N}(\text{CH}_3)_2)_3$ ).

[0049]Since the life of an oxygen radical or a TEOS dissociation molecule is quite long even if ozone does not exist in reactant gas, the same result will be obtained if the value of duty ratio is chosen suitably. The same result is obtained also when hydrides and organic compounds, such as nitrogen compounds, such as silicon inorganic compounds, ammonia, etc., such as Silang, Lynn, boron, arsenic, antimony, are made to mix into reactant gas.



[0050]Although only the high-frequency power impressed to the shower electrode 19 was changed by this example further again, if high-frequency power, a reaction chamber pressure, substrate temperature, a gas mass flow, etc. are changed synchronizing with the pulse which the pulse generator 40 generates, better step coverage nature will be obtained.

[0051]Drawing 14 is outline drawing of longitudinal section of the plasma chemistry vapor phase growth system of the 6th example of this invention. In the device of this example, the ethyl silicate (it calls the following TEOS) gas used as a silicon raw material, Carry out flow regulation of the liquid TEOS supplied from the TEOS tank which is not expressed with this figure with the mass flow type liquid flow rate regulator 175, and it is made to evaporate thoroughly with the evaporator 187, and it is mixed with the helium by which flow regulation was carried out by the flow regulator 176, and is generated. Ozone content oxygen introduces into the silent discharge type ozone generator 186 the oxygen by which flow regulation was carried out by the flow regulator 174, makes 1 to 10% of ozone contain, and is generated. Hydrogen peroxide gas is generated by carrying out bubbling of the fluid hydrogen peroxide 185 in the homiothermal container 177 with the helium by which flow regulation was carried out by the flow regulator 177. Although the concentration of hydrogen peroxide gas was adjusted at the temperature of the homiothermal container 184, it was used in 10-20 \*\* at this example. Thus, the TEOS gas, ozone containing oxygen gas, and hydrogen peroxide gas which were generated are introduced into the manifold 208 from the TEOS feed port 189, the ozone feed port 188, and the hydrogen oxide gas inlet 190. Within a manifold, it is mixed and these gases are diffused almost uniformly by hitting the gas diffusion board 192. If it hits the shower electrode 194, it will distribute still more uniformly and the surface of the substrate 207 will be sprayed. It is equipped on the SiC susceptor 196, optical heating is carried out from the heat lamp 198 through the quartz plate 197, and the substrate 207 is held at the temperature of about 200-450 \*\*. The shower electrode 194 is electrically insulated with other portions with the insulating ring 193.

The 13.56-MHz high frequency generated with RF oscillator 206 is impressed.

The exhaust pipe 199 is connected to the vacuum pump 201, and the pressure of the reaction chamber 195 is held at 0.1 - tens Torr(s).

[0052]The above devices are used in this example, The insulator layer was formed by the film formation condition of the forming temperature of 200 \*\*, forming pressure 10Torr, RF power 100W, TEOS flow 50SCCM, oxygen ( $O_2$ ) flow 1SLM, 5% of an ozone level, the hydrogen peroxide ( $H_2O_2$ ) flow 0 - 5SCCM. Drawing 16 is the figure which compared the longitudinal plane shape on the aluminum wiring 245 of the insulator layer formed by various methods. The insulator layer (henceforth a TEOS/ $O_2$  system plasma-CVD film) and drawing 16 (b) which used the plasma vapor phase growth of the conventional TEOS and oxygen ( $O_2$ ) drawing 16 (a), When a hydrogen peroxide ( $H_2O_2$ ) flow is 0SCCM among the conditions of this example (when it was got blocked and only ozone content oxygen is used). Drawing 16 (c) shows the case where a hydrogen peroxide ( $H_2O_2$ ) flow is 5SCCM among the conditions of this example. Although drawing 16 (a) and (b) show that step coverage has been considerably improved by using ozone content oxygen instead of oxygen, in the space to which an aspect ratio exceeds 1.0, it also turns out that the void (\*\*) 249 arises. From drawing 16 (c), by adding hydrogen peroxide gas ( $H_2O_2$ ) further in addition to ozone content oxygen, Generating of a void (\*\*) is lost also in the space to which an aspect ratio exceeds 1.0, and it turns out that flow shape was formed a little also in the portion of isolated aluminum wiring. The added hydrogen peroxide decomposes according to a chemical formula like a formula (1), and these results are  $H_2O_2 \rightarrow H_2O + O \dots$  (1)

It is thought that it is because the film formation precursor pseudo-liquid layer 59 is formed also in the state where generation of the film formation precursor 50 shown by drawing 3 is promoted, high-frequency power is

impressed, and plasma is irradiated in order that an oxygen radical ( $-O$ ) and water ( $H_2O$ ) may be generated and these may promote the polymerization of TEOS.

[0053]Although hydrogen peroxide was used as addition gas in this example, The same result was obtained, although the effect had a difference when hydrogen ( $H_2$ ), water ( $H_2O$ ), hydrocarbon, alcohol, a carbonyl compound, and the compound that reacts to oxygen like carboxylic acid and generates water ( $H_2O$ ) were used.

Also when hydrogen peroxide was used and an RF output was zero, the improvement of flow nature was accepted compared with the case where hydrogen peroxide is not used. Although the ethyl silicate (TEOS: chemical formula  $Si(OC_2H_5)_4$ ) was used as organic silane gas in this example, A tetramethylsilane (TMS: chemical formula  $Si(CH_3)_4$ ), Tetramethyl cyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS), Hexamethyldisilazane (HMDS), triethoxysilane (chemical formula  $SiH(OC_2H_5)_3$ ). The same result is obtained even if it uses silicon containing compounds, such as a tris dimethylamino silane (chemical formula  $SiH(N(CH_3)_2)_3$ ).

[0054]Drawing 15 is outline drawing of longitudinal section of the plasma chemistry vapor phase growth system of the 7th example of this invention. In the device of this example, the ethyl silicate (it calls the following TEOS) gas used as a silicon raw material, Carry out flow regulation of the TEOS on a fluid supplied from the TEOS tank which is not expressed with this figure with the mass flow type liquid flow rate regulator 210, and it is made to evaporate thoroughly with the evaporator 222, and it is mixed with the nitrogen gas by which flow regulation was carried out by the flow regulator 211, and is generated. Ozone content oxygen introduces into the silent discharge type ozone generator 221 the oxygen gas by which flow regulation was carried out by the flow regulator 209, makes 1 to 10% of ozone contain, and is generated. Hydrogen peroxide gas is generated by carrying out bubbling of the fluid hydrogen peroxide 220 in the homoiothermal container 219 with the helium by which flow regulation was carried out with the flow regulator 212. Although the concentration of hydrogen peroxide gas was adjusted at the temperature of the homoiothermal container 219, it was used in 10-20 \*\* at this example. Thus, the TEOS gas, ozone containing oxygen gas, and hydrogen peroxide gas which were generated are introduced into the manifold 244 from the TEOS feed port 224, the ozone feed port 223, and the hydrogen peroxide gas inlet 225. Within a manifold, it is mixed and these gases are diffused almost uniformly by hitting the gas diffusion board 227. If it hits the shower electrode 229, it will distribute still more uniformly and the surface of the substrate 243 will be sprayed. It is equipped on the SiC susceptor 231, optical heating is carried out from the heat lamp 233 through the quartz plate 232, and the substrate 243 is held at the temperature of about 200-450 \*\*. The exhaust pipe 234 is connected to the vacuum pump 236, and the pressure inside the reaction chamber 230 is held at 0.1 - tens Torr (s). The shower electrode 229 is electrically insulated with other portions with the insulating ring 228.

The 13.56-MHz high frequency generated with RF oscillator 241 is impressed.

\*\*\*\* control of the output of this RF oscillator 241 is carried out at the pulse generated with the pulse generator 242.

Periodically or intensity changes.

[0055]The above devices are used in this example, The forming temperature of 350 \*\*, forming pressure 10Torr, RF frequency of 13.56 MHz, RF power 100W, the pulse frequency of 1 Hz, D= 30% of duty ratio, TEOS flow 50SCCM, oxygen ( $O_2$ ) flow 1SLM, 5% of an ozone level, hydrogen peroxide. ( $H_2O_2$ ) The insulator layer was formed by the film formation condition of the flow 0 - 5SCCM. Drawing 17 shows the longitudinal plane shape on the aluminum wiring 251 of the insulator layer formed by the film formation condition of this example. According to this example, a figure shows that it not only embeds the space part in which an aspect ratio exceeds 1.0, but flow

shape is obtained and the insulator layer which has a smooth surface state is obtained.

[0056]In this example, although 13.56 MHz was used as frequency of a RF oscillator, if low frequency waves, such as 450 Hz, are added, a still better result will be obtained like Example 1 of this invention. In this example, although ON-OFF of RF power was performed using the pulse generator, even if it repeats the state where it does not glare [ an exposure and ] of plasma, the same result is obtained using a device like drawing 6. Although the ethyl silicate (TEOS: chemical formula  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) was used as organic silane gas in this example, A tetramethylsilane (TMS: chemical formula  $\text{Si}(\text{CH}_3)_4$ ), Tetramethyl cyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS), Hexamethyldisilazane (HMDS), triethoxysilane (chemical formula  $\text{SiH}(\text{OC}_2\text{H}_5)_3$ ), The same result is obtained even if it uses silicon containing compounds, such as a tris dimethylamino silane (chemical formula  $\text{SiH}(\text{N}(\text{CH}_3)_2)_3$ ).

[0057]Drawing 18 is outline drawing of longitudinal section of the plasma chemistry vapor phase growth system of the 8th example of this invention. Octamethylcyclotetrasiloxane which serves as a silicon raw material in the device of this example (it calls the following OMCTS.) A chemical formula is  $\text{Si}_4\text{O}_{12}\text{C}_8\text{H}_{24}$ . Gas, Carry out flow regulation of the liquid OMCTS supplied from the OMCTS tank which is not expressed with this figure with the mass flow type liquid flow rate regulator 255, and it is made to evaporate thoroughly with the evaporator 265, and it is mixed with the nitrogen gas by which flow regulation was carried out by the flow regulator 256, and is generated. Ozone content oxygen introduces into the silent discharge type ozone generator 264 the oxygen gas by which flow regulation was carried out by the flow regulator 254, makes 0.1 to 1.0% of ozone contain, and is generated. Ammonia gas is supplied from  $\text{HN}_3$  gas bomb which is not expressed with this figure, and flow regulation is carried out by flow control term 257. Thus, the OMCTS gas, ozone containing oxygen gas, and ammonia gas which were generated are introduced into the manifold 269 from the OMCTS feed port 267, the ozone feed port 268, and the  $\text{NH}_3$  feed port 266. Within a manifold, it is mixed and these gases are diffused almost uniformly by hitting the gas diffusion board 271. If it hits the shower electrode 273, it will distribute still more uniformly and the surface of the substrate 275 will be sprayed. It is equipped on the SiC susceptor 276, optical heating is carried out from the heat lamp 278 through the quartz plate 277, and the substrate 275 is held at the temperature of about 200-450 \*\*. The exhaust pipe 279 is connected to the vacuum pump 281, and the pressure inside the reaction chamber 274 is held at 0.1 - the suitable value of tens Torr(s). The shower electrode 273 is electrically insulated with other portions with the insulating ring 272.

The 13.56-MHz high frequency generated by the RF generator 286 is impressed.

The output of this RF oscillator 286 is controlled by the pulse generated with the pulse generator 287.

Periodically or intensity changes.

[0058]In this example, using the above devices, the forming temperature of 300 \*\*, forming pressure 1.0Torr, RF frequency of 13.56 MHz, RF power 300W, the pulse frequency of 0.2 Hz (pulse cycle 5 seconds), The insulator layer was formed by the film formation condition of D= 20% of duty ratio, OMCTS flow 50SCCM, oxygen ( $\text{O}_2$ ) flow 0.1SLM, 1% of an ozone level, and ammonia ( $\text{NH}_3$ ) flow 1.0SLM.

[0059]The film growth rate of about 1200 Å / min was obtained as a result, and step coverage was not less than 90%. The presentation is SiON whose nitrogen content is 5 to 25%.

It turned out that a film Nakamizu daily dose is also an insulator layer good at 1% or less.

[0060]The membrane formation mechanism of the insulator layer of this example is explained as follows. First, the heat CVD reaction of ozone and OMCTS is performed in the state of OFF of RF power. The  $\text{SiO}_2$  film having

contained quite many moisture is formed at this reaction. Next, if RF power is set to ON, ammonia plasma will occur. If the  $\text{SiO}_2$  film formed by the heat CVD reaction is put to this ammonia plasma, a nitrogen ion will be poured in and it will be considered nitriding. The plasma-CVD reaction has also produced the time of ON of RF power simultaneously.

Since Si, O, N, and H are contained in reactant gas, a SiON film is formed.

In this example, DEPORETO of the plasma-CVD reaction to which DEPORETO of the heat CVD reaction of ozone and OMCTS turned ON about 1000 A / min, and RF power is 2000 A / min, Since the time of RF power OFF is 4 seconds, it means putting the  $\text{SiO}_2$  film of about 125-A thickness to ammonia plasma. The artificer of this invention is checking nitriding [ the  $\text{SiO}_2$  film of thickness of this level / ammonia plasma ] easily.

And it is also checking that composition distribution and membraneous distribution hardly arise in a thickness direction by ON-OFF of RF power.

[0061]In this example, although 13.56 MHz was used as frequency of a RF oscillator, if low frequency waves, such as 450 Hz, are added, a still better result will be obtained like Example 1 of this invention. In this example, although ON-OFF of RF power was performed using the pulse generator, even if it repeats the state where it does not glare [ an exposure and ] of plasma, the same result is obtained using a device like drawing 6. Although octamethylcyclotetrasiloxane (OMCTS) was used as organic silane gas in this example, An ethyl silicate ( $\text{TEOS:Si}(\text{OC}_2\text{H}_5)_4$ ), A tetramethylsilane ( $\text{TMS:Si}(\text{CH}_3)_3$ ), The same result is obtained even if it uses silicon containing compounds, such as tetramethyl cyclotetrasiloxane (TMCTS), hexamethyldisilazane (HMDS), and triethoxysilane ( $\text{SiH}(\text{OC}_2\text{H}_5)_3$ ). As organic silane gas, a tris dimethylamino silane ( $\text{SiH}(\text{N}(\text{CH}_3)_2)_3$ ), a tris diethylamino silane ( $\text{SiH}(\text{N}(\text{C}_2\text{H}_5)_2)_3$ ), etc., Nitrogen content can be raised if the compound which has Si-N combination is used. Although ammonia ( $\text{NH}_3$ ) was used in this example as gas made to generate the plasma which pours in nitrogen, the effect that the mixed gas of  $\text{N}_2$ ,  $\text{N}_2$ , and  $\text{H}_2$  is also the same is acquired.

[0062]Drawing 19 is drawing of longitudinal section showing the outline of the plasma chemistry vapor phase growth system of the 9th example of this invention.

[0063]Ammonia gas  $\text{NH}_3$  by which flow regulation was carried out to the ion source cave 305 by the flow regulator 288, Nitrogen gas  $\text{N}_2$  by which flow regulation was carried out to laughter gas  $\text{N}_2\text{O}$  by which flow regulation was carried out by the flow regulator 289 by the flow regulator 290 is supplied, and the pressure is maintained at  $p=100\text{mTorr}$ . Microwave with a frequency of 2.45 GHz is supplied via the waveguide 299 and the transmission window 298 from the microwave power supply 300. By the 875 gauss magnetic field which the main electromagnet coil 303 makes, within the ion source cave 305, the electron cyclotron resonance (ECR) has happened and the high plasma of an ionization rate occurs. With the emission magnetic field and the auxiliary coil 1.304 of the main electromagnet 303, the oxygen ion, nitrogen ion, and hydrogen ion which are generated here are pulled out to the reaction chamber 309, pass through the crevice between the grids 307, and it is irradiated with them to the substrate 310. The grid 307 rebounds ion with the voltage to impress, or is carrying out the duty of the shutter which makes it pass.

[0064]The TDEAS gas used as a silicon raw material the TDEAS gas which evaporated from TDEAS(fluid)318 kept warm in the homoiothermal container 317 kept at 80 \*\*, Flow regulation is carried out by the flow regulator 292, and it is mixed with the nitrogen gas by which flow regulation was carried out by the flow regulator 291, and is introduced from the source gas feed port 308 to a reaction chamber, and a substrate face is sprayed. Here, piping and the source gas feed port 308 which are connected with the source gas feed port 308 from the homoiothermal container 317 containing TDEAS318 are maintained at the constant temperature of not less than

80 \*\*. It is equipped with the substrate 310 on the susceptor 312, and it is heated by 300 \*\* with the heater 315. The pressure of the reaction chamber is maintained at about 1 mTorr by the vacuum pump 316.

[0065]In the plasma CVD device of this example, first, the microwave power supply 300 is operated, an 875 gauss magnetic field is generated with a main electromagnet coil, ECR resonance is produced and the plasma which consists of nitrogen gas, ammonia gas, and laughter gas in the ion source cave 305 is generated. It is suitable, and it comes out, and is made the small value, and the exposure of plasma makes the current sent through the auxiliary coils 1 and 304 and the auxiliary coils 2 and 311 the grade which generates the magnetic field which faces to a substrate from an ion source and which becomes uniform. The ion electrified in positive [, such as oxygen ion  $O^+$  / which impresses positive voltage to the grid 307 and exists in plasma / , nitrogen ion  $N^+$  , and hydrogen ion  $H^+$  , ] recoils by a positive electric field, and the substrate 310 is kept from being irradiated. In this state, only neutral active species (radical) and molecule which were generated in the plasma in the ion source cave 305 are supplied to the substrate 310 surface. Here, if TDEAS gas is supplied, the thermal reaction activated with neutral active species (radical) will occur, and a SiON film with sufficient step coverage will be formed. In this example, about 10 nm of SiON films by this thermal reaction were formed. Next, voltage impressed to the grid 307 is made into zero or a negative small value, and it is made for the just electrified ion to be irradiated by the surface of the substrate 310. Then, by receiving an ion bombardment, the moisture and carbon in a film \*\*\*\* and the SiON film formed by thermal reaction turns into a plasma-CVD film and a good SiON film of membraneous quality which has equivalent membraneous quality. In a substrate face, the plasma chemical reaction has also occurred and plasma CVD and a SiON film are also formed simultaneously. Then, the number of ion which will be irradiated with it by the substrate 310 if the voltage impressed to the grid 307 is changed with the cycle of 1 to about 10 seconds will change periodically, and formation of heat CVD and the SiON film by thermal reaction and refining to plasma CVD and a SiON film will be performed by turns. As a result, plasma CVD and a SiON film excellent in step coverage and a level difference embedding positive are formed. Since the reaction chamber pressure is especially set to about 1 mTorr by this example, the embedding of the big slot on the aspect ratio is also possible.

[0066]Although the recoil electric field by impressing positive voltage to the grid 307 was used in the above-mentioned example as a means to change the ion irradiated by the substrate 310, The mirror type magnetic field by the auxiliary coils 1 and 304, the cusp type magnetic field formed with the auxiliary coils 2 and 311, and the recoil electric field formed in the susceptor 312 by impressing positive voltage from the bias application power supply 313 may be used. Although not shown in drawing 19, the same result is obtained even if it uses a mechanical shutter. However, when it is made structure which bars radical diffusion using a mechanical shutter etc., it cannot be overemphasized that it is better to supply a radical near the substrate using a radical generator, to promote thermochemistry vapor phase epitaxy, and to have promoted growth of the heat CVD film.

[0067]In the above-mentioned example, although the electron cyclotron resonance type (ECR) ion source was used as an ion source, if the intensity of ion can be changed, it will not be based on the form but the same result will be obtained.

[0068]Although the tris diethylamino silane (TDEAS: chemical formula  $SiH(N(C_2H_5)_2)_3$ ) was used as organic silane gas in this example, An ethyl silicate (TEOS: chemical formula  $Si(OC_2H_5)_4$ ), A tetramethylsilane (TMS: chemical formula  $Si(CH_3)_4$ ), Tetramethyl cyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS), Hexamethyldisilazane (HMDS), triethoxysilane (chemical formula  $SiH(OC_2H_5)_3$ ), The same result is obtained even if it uses silicon containing compounds, such as a tris dimethylamino silane (chemical formula  $SiH(N(CH_3)_2)_3$ ).

[0069]The same result is obtained also when hydrides and organic compounds, such as nitrogen compounds, such as silicon inorganic compounds, ammonia, etc., such as Silang, Lynn, boron, arsenic, antimony, are made to mix into reactant gas. Although ammonia ( $\text{NH}_3$ ) was used as gas made to generate plasma in this example, the effect that the mixed gas of  $\text{N}_2$ ,  $\text{N}_2$ , and  $\text{H}_2$  is also the same is acquired.

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[Translation done.]

\* NOTICES \*

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

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## DESCRIPTION OF DRAWINGS

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### [Brief Description of the Drawings]

[Drawing 1]Outline drawing of longitudinal section of the plasma chemistry vapor phase growth system showing the 1st example of this invention.

[Drawing 2]The figure which expresses operation of the plasma chemistry vapor phase growth system of drawing 1 about the temporal change of impression high-frequency power, the number of oxygen ion, and an ozone level.

[Drawing 3]The model figure showing the outline of the principle of this invention.

[Drawing 4]Drawing of longitudinal section showing the growth process of the time progress and the film at the time of performing operation like drawing 2.

[Drawing 5]The high frequency ON time at the time of performing operation like drawing 2 ( $t_{ON}$ ) is [ comparatively (duty D) and ] a related figure of a film growth rate, step coverage, and the absorption index of an OH radical.

[Drawing 6]The 2nd outline top view and drawing of longitudinal section of a reaction chamber of Example 2 of a plasma chemistry vapor phase growth system. [ of this invention ]

[Drawing 7]Drawing of longitudinal section showing the outline of the plasma chemistry vapor phase growth system of the 3rd example of this invention.

[Drawing 8]Drawing of longitudinal section showing the interlayer insulation film flattening method of the aluminum multilevel interconnection of the 4th example of this invention.

[Drawing 9]The schematic diagram of the conventional plasma vapor phase growth system.

[Drawing 10]The variation diagram to the membrane formation time of the high-frequency power in the conventional method of acting plasma chemistry vapor phase growth, and ozone and the thermochemistry vapor phase growth of TEOS by turns impressed to a shower electrode, the number of oxygen ion in plasma, and the ozone level in material gas.

[Drawing 11]Drawing of longitudinal section showing the film growth at the time of performing plasma chemistry vapor phase growth and ozone thermochemistry vapor phase growth by turns.

[Drawing 12]Drawing of longitudinal section showing the formation method of the conventional flattening insulator layer for multilevel interconnection using plasma chemistry vapor phase growth and the silica applying method.

[Drawing 13]Temporal change figures which use the plasma chemistry vapor phase growth system of the 1st example of drawing 1, such as high-frequency power which shows the method of operation of the 5th example.

[Drawing 14]Drawing of longitudinal section showing the outline of the plasma chemistry vapor phase growth system of the 6th example of this invention.

[Drawing 15]Drawing of longitudinal section showing the outline of the plasma chemistry vapor phase growth system of the 7th example of this invention.

[Drawing 16]Drawing of longitudinal section showing the step coverage of the insulator layer formed using the plasma vapor phase growth of the 6th example of this invention.

[Drawing 17] Drawing of longitudinal section showing the step coverage of the insulator layer formed using the plasma vapor phase growth of the 7th example of this invention.

[Drawing 18] Drawing of longitudinal section showing the outline of the plasma chemistry vapor phase growth system of the 8th example of this invention.

[Drawing 19] Drawing of longitudinal section showing the outline of the plasma chemistry vapor phase growth system of the 9th example of this invention.

[Description of Notations]

1 and 2 Flow regulator

3 Liquid flow rate regulator

4 and 5 Flow regulator

6-10 Valve

11 Ozone generator

12 Evaporator

13 Ozone feed port

14 TEOS feed port

15 Manifold

16 helium feed port

17 Gas diffusion board

18 Insulating ring

19 Shower electrode

20 Reaction chamber

21 SiC susceptor

22 Quartz plate

23 Heat lamp

24 Exhaust pipe

25 Butterfly valve

26 Vacuum pump

27 Pulse motor

28 Substrate

29 Thermo sensor

30 Pressure sensor

31 Valve opening regulator

32 Heat lamp controller

33 Preamplifier

34 Preamplifier

35 Low pass filter

36 450kHz RF generator

37 Matching box

38 High-pass filter

39 13.56MHz RF generator

40 Pulse generator

41 Process controller

42 Change of the number of ozone molecules

43 Change of the number of oxygen ion

44 Change of high-frequency power



45 Electron  
46 TEOS dissociation molecule  
47 Oxygen ion  
48 The drift of oxygen ion  
49 Diffusion of a TEOS dissociation molecule  
50 Film formation precursor  
51 Formation film  
52 Substrate  
53 Diffusion of TEOS  
54 TEOS  
55 Oxygen radical  
56 Ozone molecule  
57 Diffusion of an oxygen radical  
58 Diffusion of an ozone molecule  
59 Film formation precursor pseudo-liquid layer  
60 The 1st plasma-CVD film  
61 Aluminum wiring  
62 The 1st heat CVD film  
63 The 2nd plasma-CVD film  
64 The formation film before the 2nd plasma-CVD film growth  
65 The 2nd heat CVD film  
66 The formation film after the 2nd plasma-CVD film growth  
67 The 3rd plasma-CVD film  
68 The formation film before the 3rd plasma-CVD film growth  
69 Substrate  
70 Heat CVD field  
71 Susceptor  
72 Reaction chamber  
73 TEOS feed port  
74 Oxygen feed port  
75 Ozone feed port  
76 Insulator  
77 RF introduction terminal  
78 Shower electrode  
79 Axis of rotation  
80 Heater  
81 Shower injector  
82 Insulating ring  
83 Gas distribution plate  
166 Plasma-CVD field  
84 Microwave power supply  
85 Waveguide  
86 Transmission window  
87 Flow regulator  
88 Flow regulator

89 Valve  
90 Valve  
91 Ar feed port  
92 O<sub>2</sub> feed port  
93 Ion source cave  
94 94' Main electromagnet coil  
95 Reaction chamber  
96 and 96' auxiliary coil  
97 Ozone feed port  
98 Ozone generator  
99 Valve  
100 Valve  
101 Flow regulator  
102,102' Reflective magnetic coil  
103 Flow regulator  
104 Exhaust pipe  
105 Vacuum pump  
106 Substrate  
107 TEOS feed port  
108 Ar feed port  
109 Susceptor  
110 Heater  
111 TEOS  
112 A homoiothermal container  
113 Flow regulator  
164 Coil driving source  
168 Bias application device  
114 Aluminum wiring  
115 Substrate  
167 The CVD film of this invention (progress)  
116 The CVD film of this invention  
117 Resist  
118 The interlayer film by which flattening was carried out  
119 Flow regulator  
120 Flow regulator  
121 Valve  
122 Valve  
123 Flow regulator  
124 Valve  
125 Flow regulator  
126 Valve  
127 Valve  
128 Flow regulator  
129 13.56MHz RF generator

130 High-pass filter  
131 TEOS  
132 Bubbler  
133 450kHz RF generator  
134 Low pass filter  
135 Matching box  
136 Manifold  
137 Oxygen and an ozone feed port  
138 TEOS feed port  
139 helium feed port  
140 Gas diffusion board  
141 Insulating ring  
142 Shower electrode  
143 Reaction chamber  
144 SiC susceptor  
145 Quartz plate  
146 Heat lamp  
147 Substrate  
148 Exhaust pipe  
149 Vacuum pump  
165 Ozone generator  
150 The temporal change of an ozone level  
151 Change of the number of oxygen ion  
152 Change of high-frequency power  
153 Aluminum wiring  
154 The 1st plasma-CVD film  
155 The 1st heat CVD film  
156 The 2nd plasma-CVD film  
158 Aluminum wiring  
159 Plasma-CVD film  
160 Silica coating film (1-time spreading)  
161 Silica coating film (multiple-times spreading)  
162 After [ etchback ] silica coating film  
163 Plasma-CVD film  
169 Change of 13.56MHz high-frequency power  
170 Change of 450kHz high-frequency power  
171 Change of ion current density  
172 Change of average ion energy  
173 Change of a growth rate  
174 Flow regulator  
175 Liquid flow rate regulator  
176-178 Flow regulator  
179-183 Valve  
184 A homoiothermal container

185 Hydrogen peroxide ( $\text{H}_2\text{O}_2$ )  
186 Ozone generator  
187 Evaporator  
188 Ozone feed port  
189 TEOS feed port  
190  $\text{H}_2\text{O}_2$  feed port  
191 helium feed port  
192 Gas diffusion board  
193 Insulating ring  
194 Shower electrode  
195 Reaction chamber  
196 SiC susceptor  
197 Quartz plate  
198 Heat lamp  
199 Exhaust pipe  
200 Bara fly valve  
201 Vacuum pump  
202 BARUSU motor  
203 Valve opening regulator  
204 Pressure sensor  
205 Preamplifier  
206 RF oscillator  
207 Substrate  
208 Manifold  
209 Flow regulator  
210 Liquid flow rate regulator  
211-213 Flow regulator  
214-218 Valve  
219 A homoiothermal container  
220 Hydrogen peroxide ( $\text{H}_2\text{O}_2$ )  
221 Ozone generator  
222 Evaporator  
223 Ozone feed port  
224 TEOS feed port  
225  $\text{H}_2\text{O}_2$  feed port  
226 helium feed port  
227 Gas diffusion board  
228 Insulating ring  
229 Shower electrode  
230 Reaction chamber  
231 SiC susceptor  
232 Quartz plate  
233 Heat lamp

234 Exhaust pipe  
235 Butterfly valve  
236 Vacuum pump  
237 Pulse motor  
238 Valve opening regulator  
239 Pressure sensor  
240 Preamplifier  
241 RF oscillator  
242 Pulse generator  
243 Substrate  
244 Manifold  
245 Aluminum wiring  
246 TEOS/O<sub>2</sub> system CVD film  
247 The insulator layer of this example (H<sub>2</sub>O<sub>2</sub> flow = 0SCCM)  
248 The insulator layer of this example (H<sub>2</sub>O<sub>2</sub> flow = 5SCCM)  
249 Void (\*\*)  
250 Substrate  
251 Aluminum wiring  
252 The insulator layer of this example  
253 Substrate  
254 Flow regulator  
255 Liquid flow rate regulator  
256-258 Flow regulator  
259-263 Valve  
264 Ozone generator  
265 Evaporator  
266 NH<sub>3</sub> feed port  
267 OMCTS feed port  
268 Ozone feed port  
269 Manifold  
270 N<sub>2</sub> feed port  
271 Gas diffusion board  
272 Insulating ring  
273 Shower electrode  
274 Reaction chamber  
275 Substrate  
276 SiC susceptor  
277 Quartz plate  
278 Heat lamp  
279 Exhaust pipe  
280 Butterfly valve  
281 Vacuum pump  
282 Pulse motor

283 Valve opening regulator  
284 Pressure sensor  
285 Preamplifier  
286 RF oscillator  
287 Pulse generator  
288-292 Flow regulator  
293-297 Valve  
298 Transmission window  
299 Waveguide  
300 Microwave power supply  
301 N<sub>2</sub> feed port  
302 NH<sub>3</sub>, an N<sub>2</sub>O feed port  
303 Main magnet coil  
304 Auxiliary coil 1  
305 Ion source cave  
306 Grid voltage control power source  
307 Grid  
308 Source gas feed port  
309 Reaction chamber  
310 Substrate  
311 Auxiliary coil 2  
312 Susceptor  
313 Bias application power supply  
314 Exhaust pipe  
315 Heater  
316 Vacuum pump  
317 A homoiothermal container  
318 TDEAS

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[Translation done.]

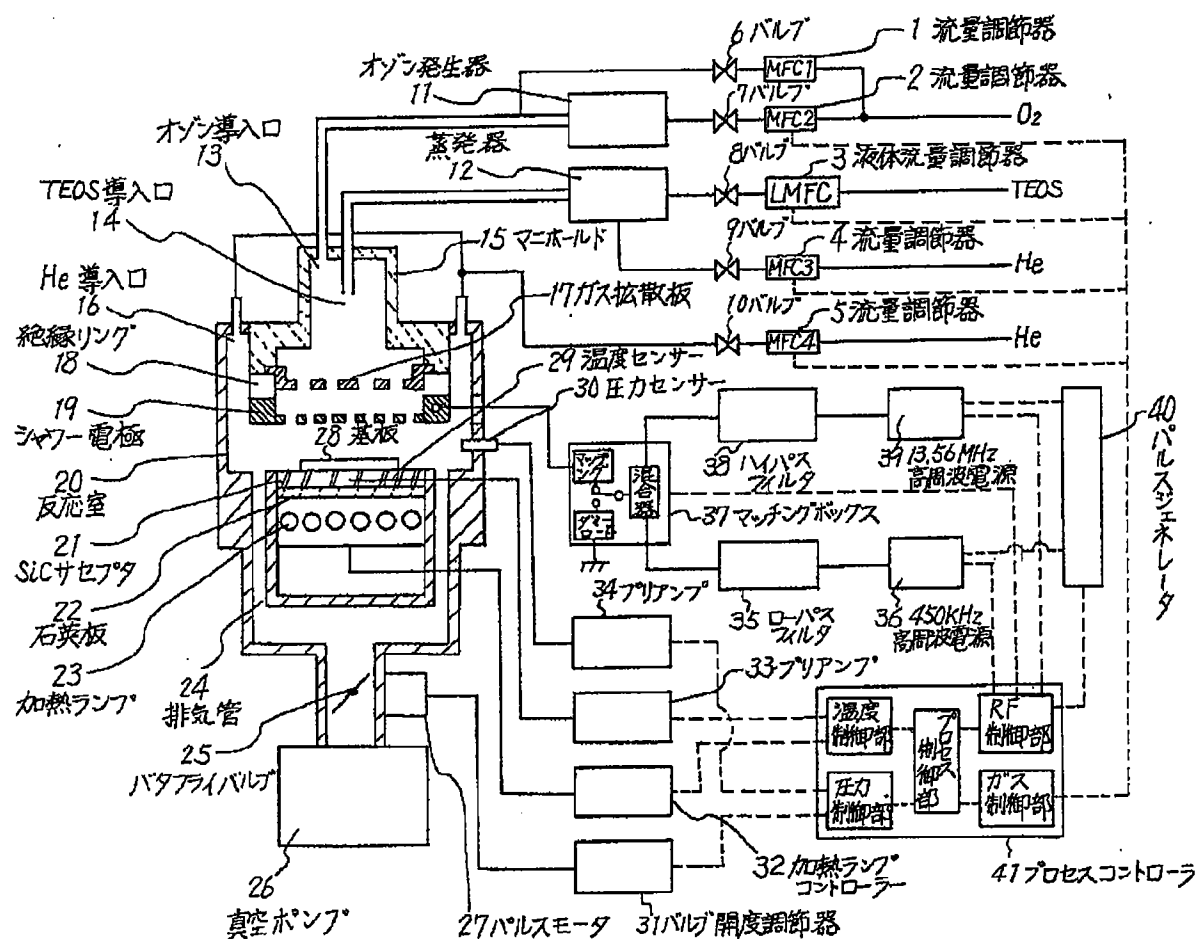
## \* NOTICES \*

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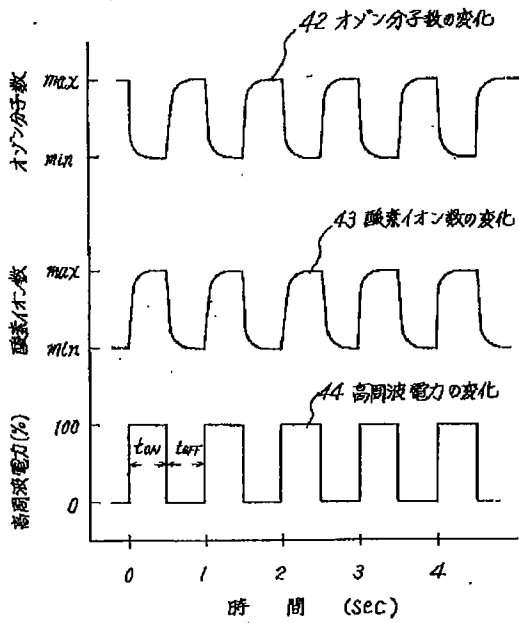
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DRAWINGS

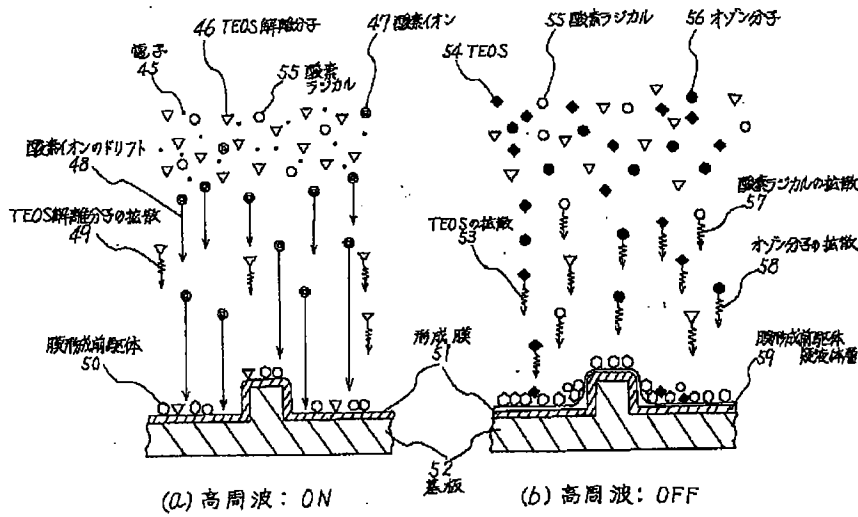
[Drawing 1]



[Drawing 2]

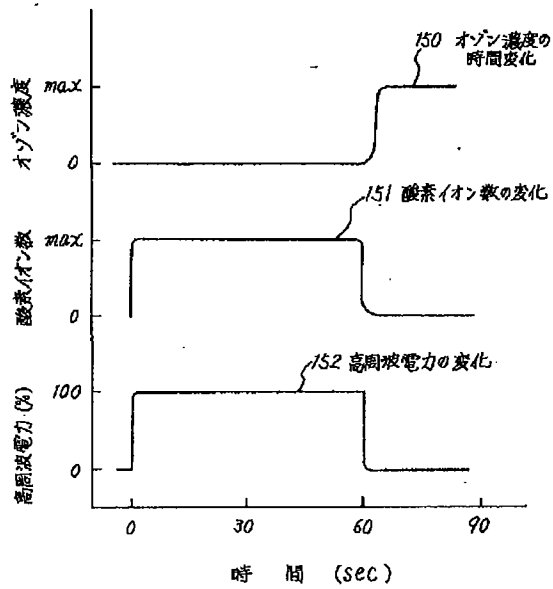


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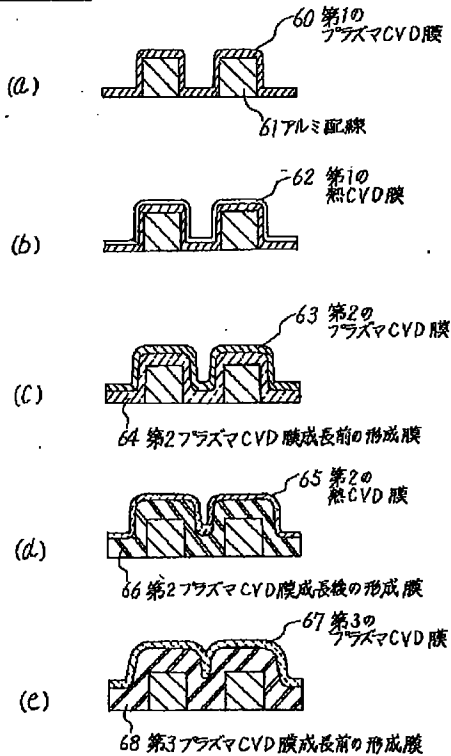


[Drawing 10]

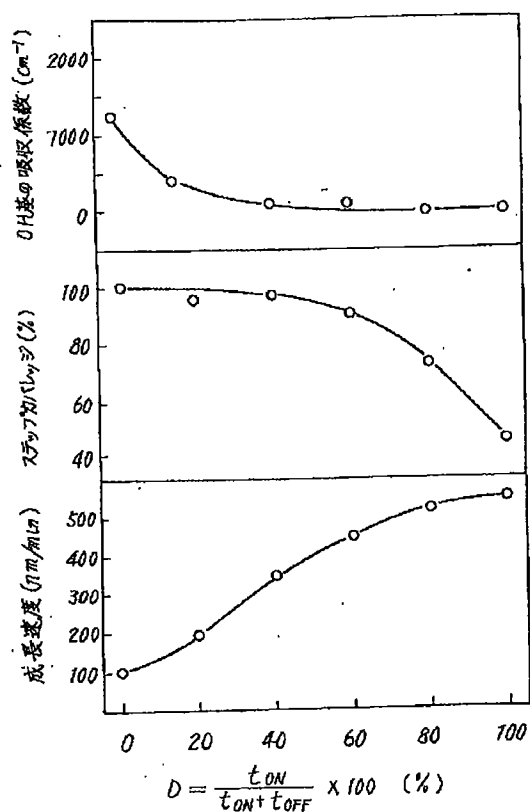




[Drawing 4]

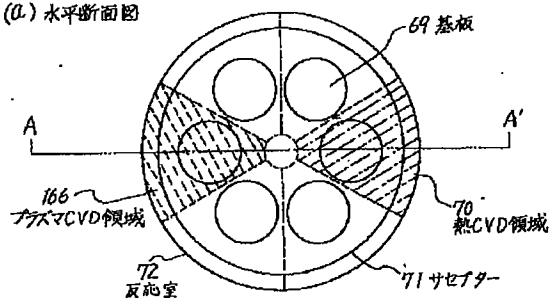


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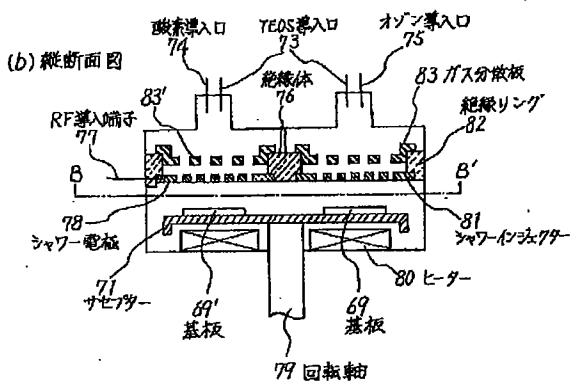


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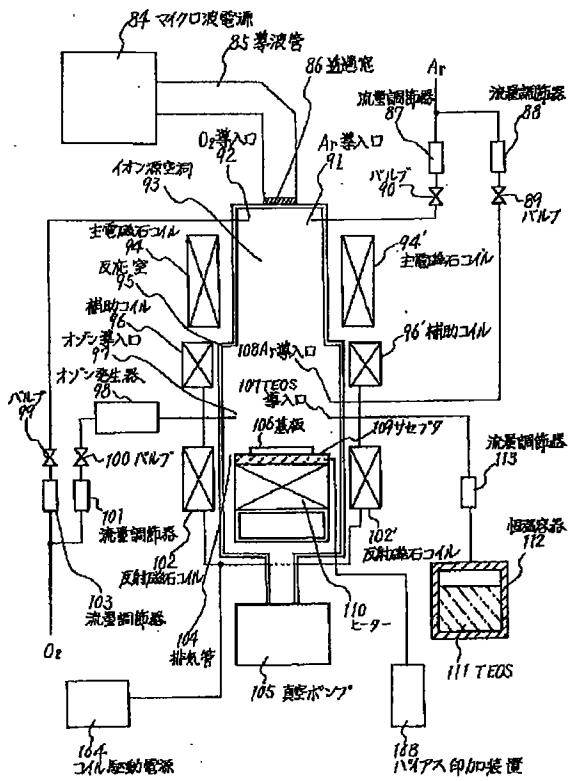
(a) 水平断面図



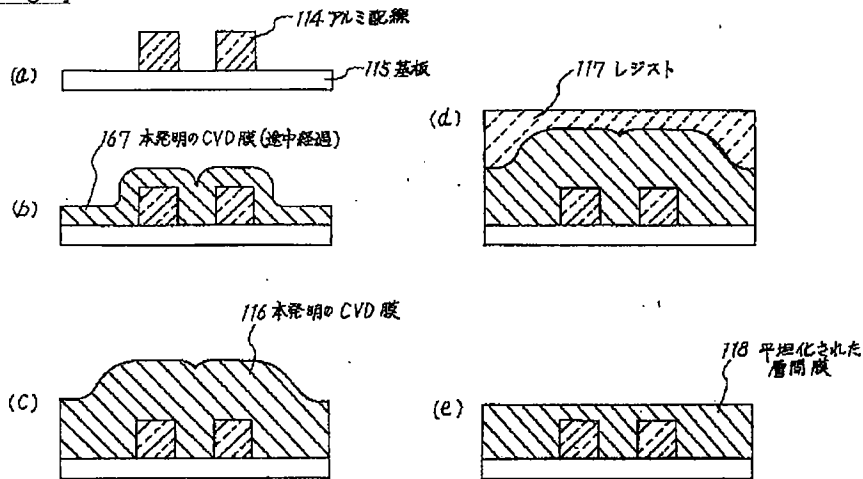
(b) 縦断面図



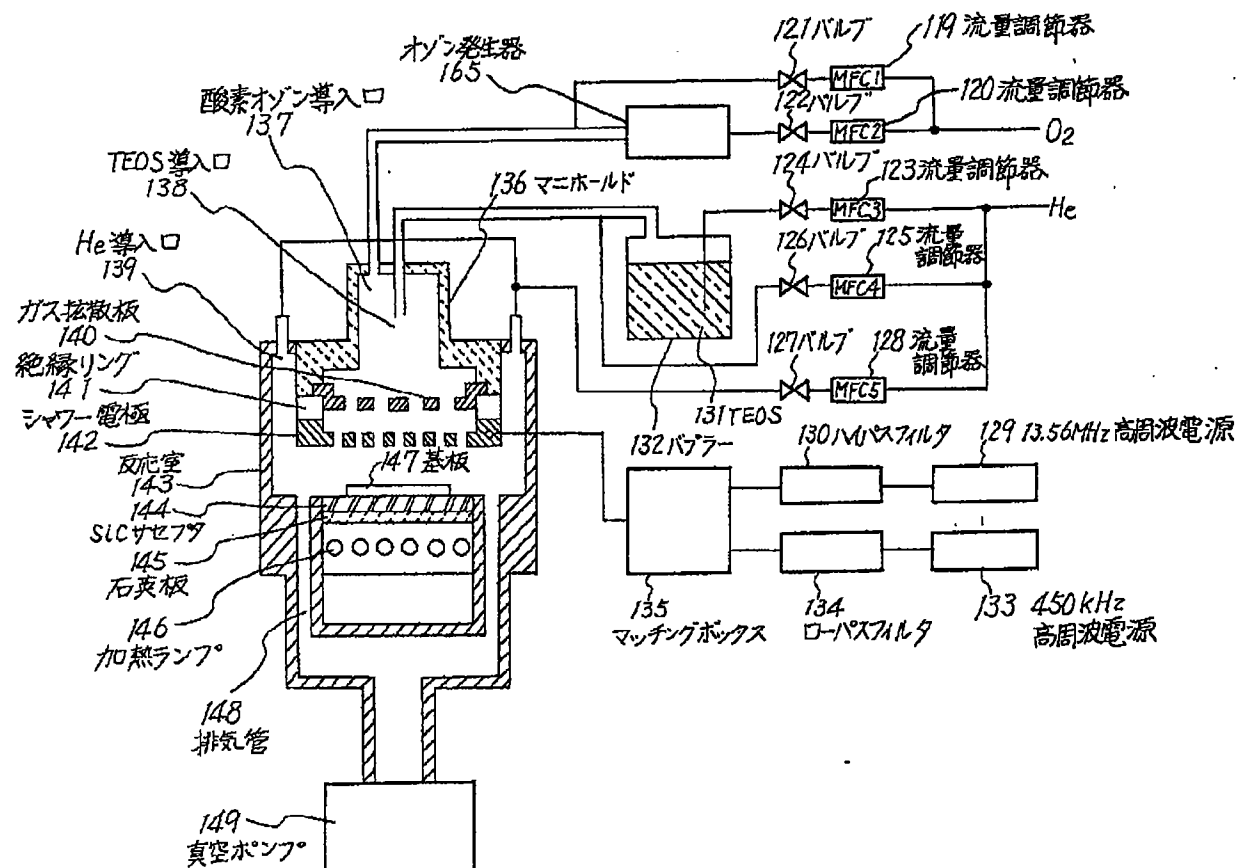
[Drawing 7]



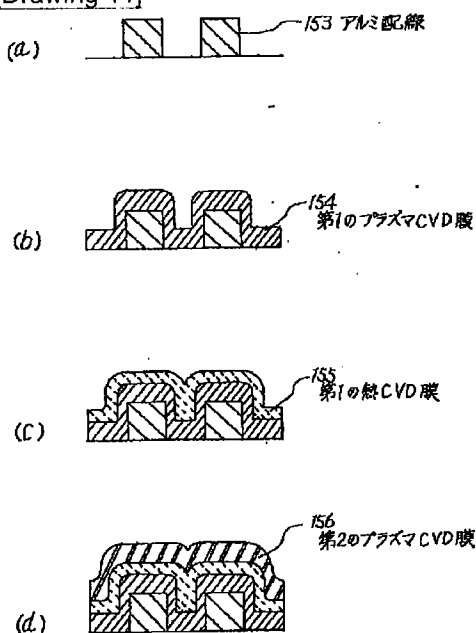
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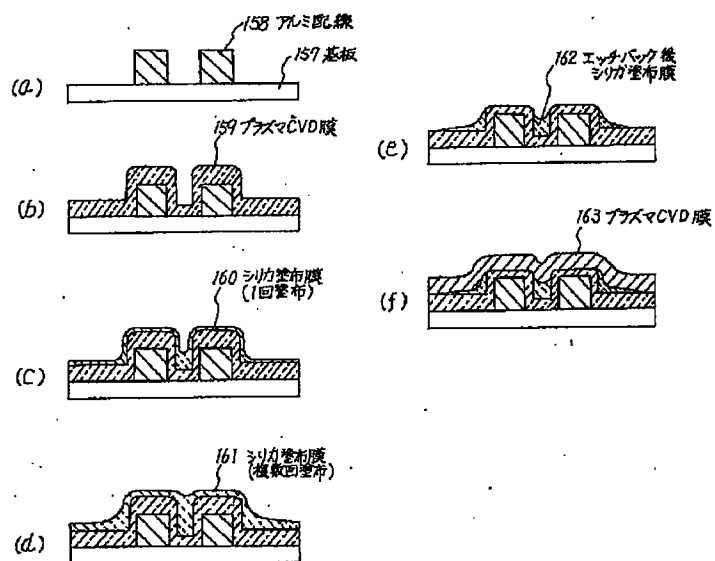
[Drawing 9]



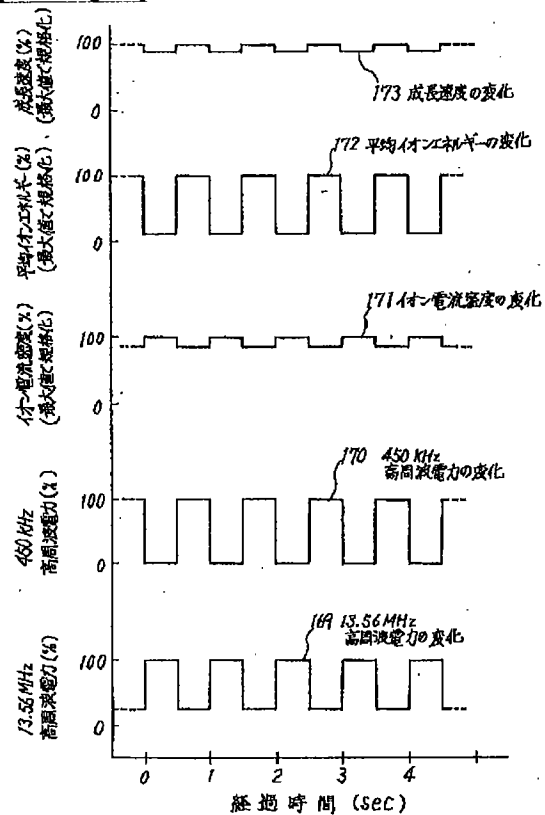
[Drawing 11]



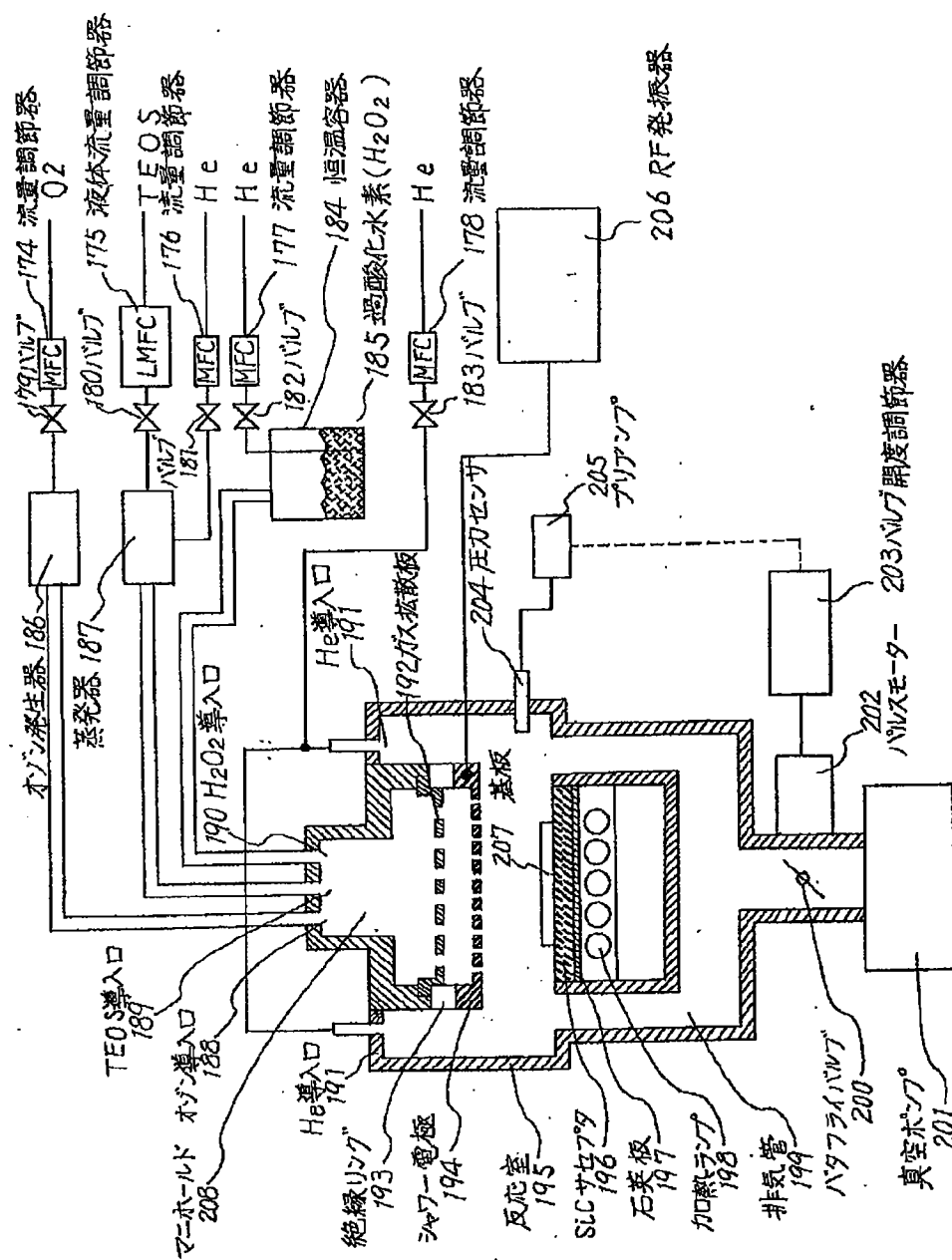
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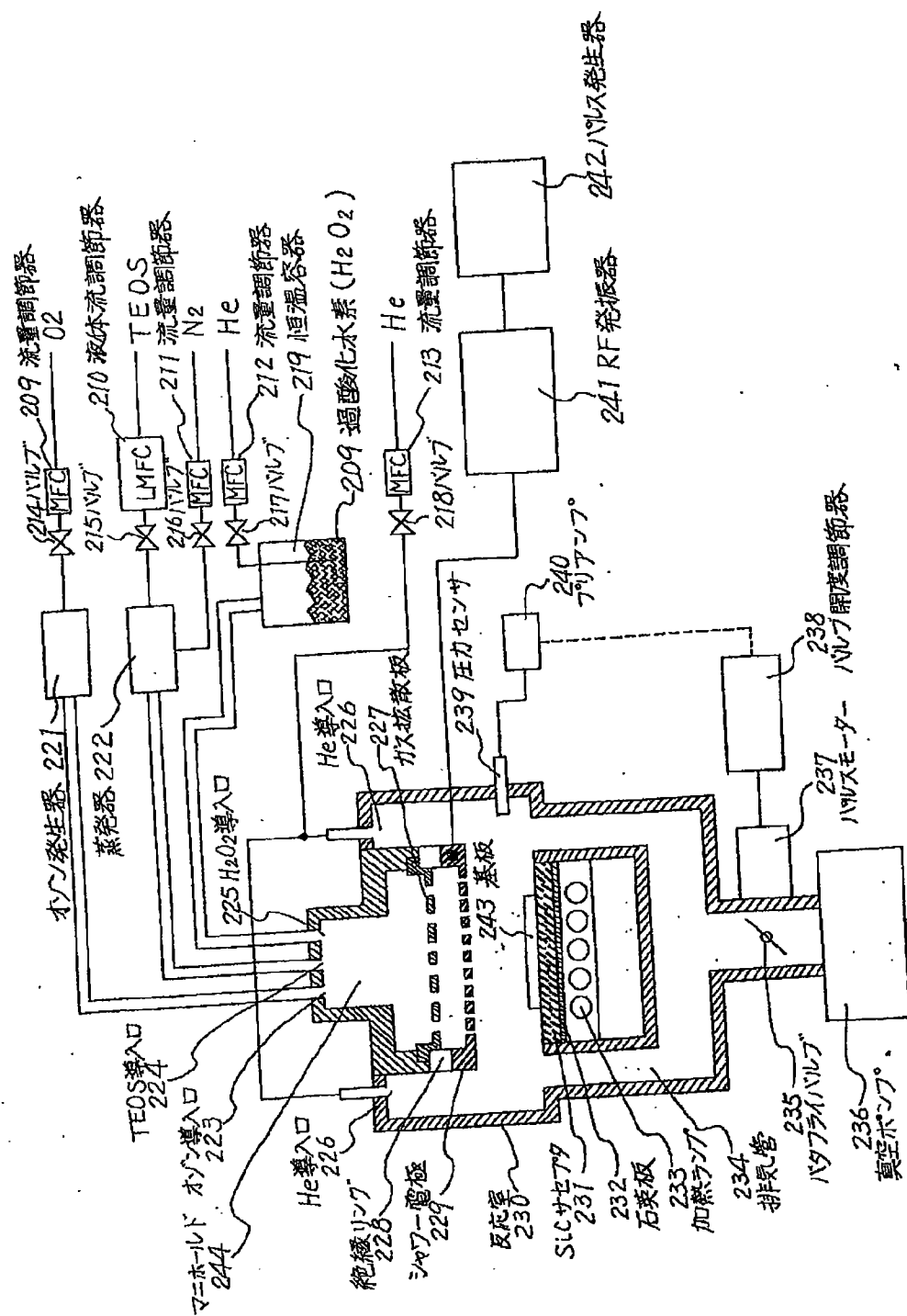
[Drawing 13]



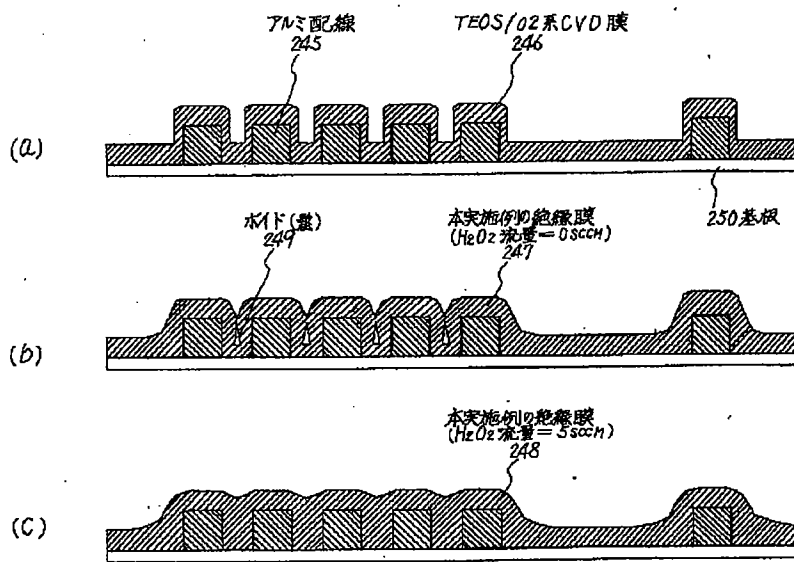
[Drawing 14]



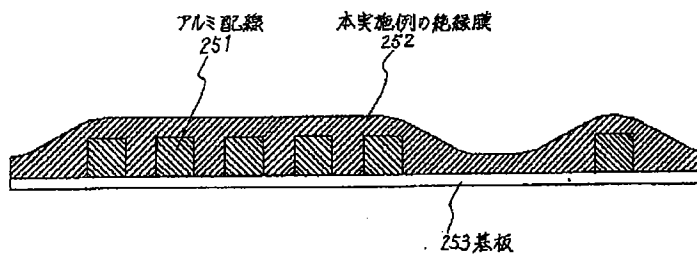
[Drawing 15]



[Drawing 16]

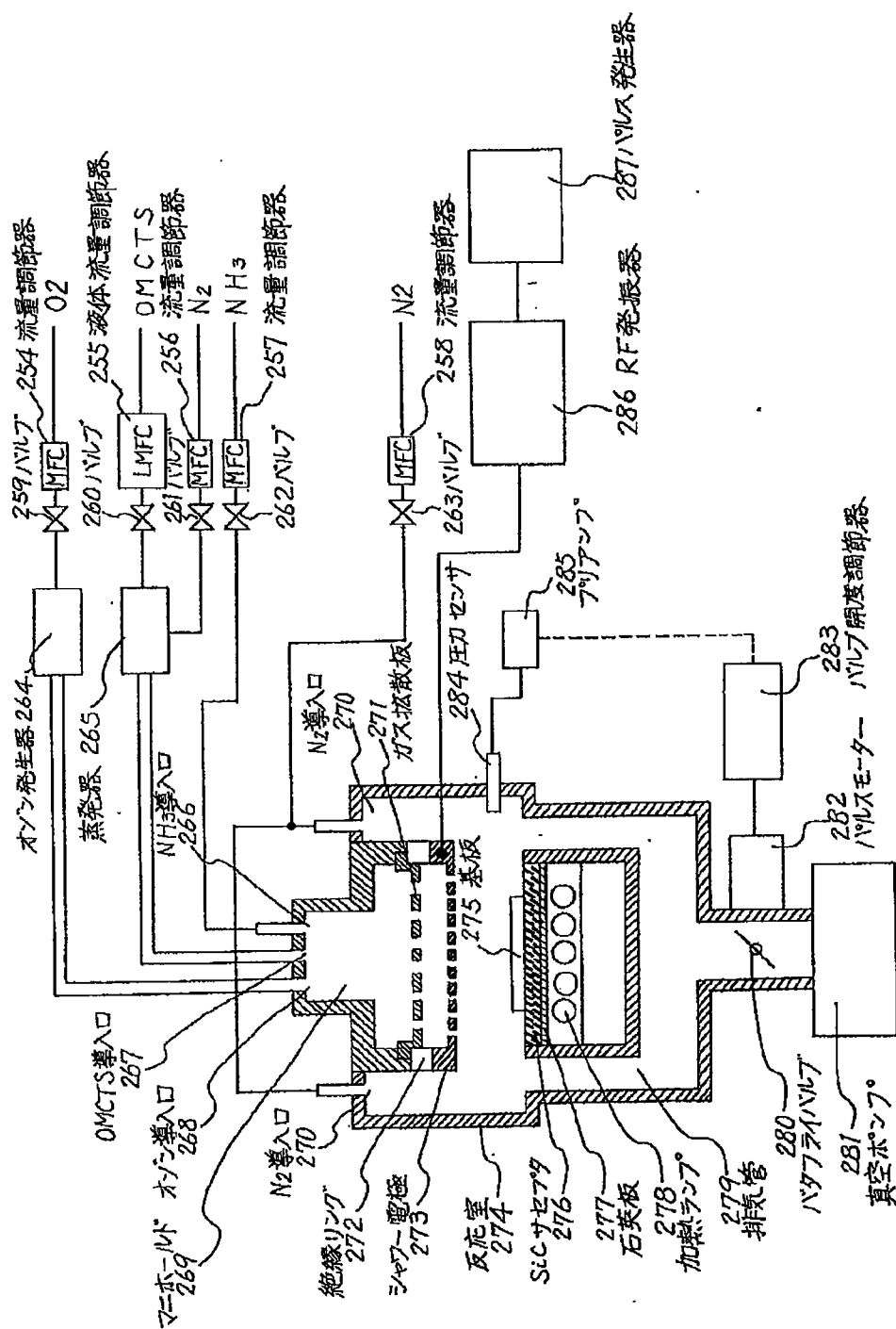


[Drawing 17]

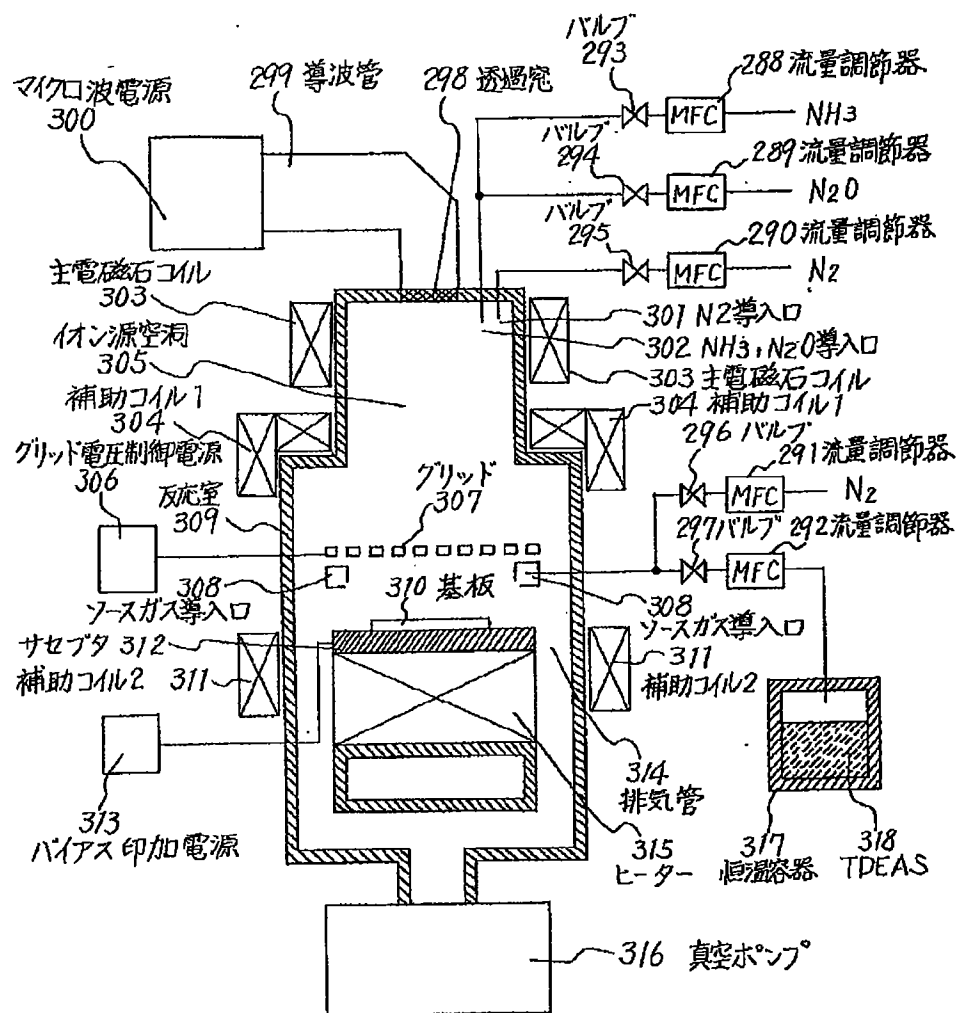


[Drawing 18]





[Drawing 19]



[Translation done.]

## PATENT ABSTRACTS OF JAPAN

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(51)Int. Cl.

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C23C 16/50  
C30B 25/14  
C30B 25/16  
H01L 21/316  
H01L 21/90

(21)Application number : 04-320973

(71)Applicant : NEC CORP

(22)Date of filing : 30.11.1992

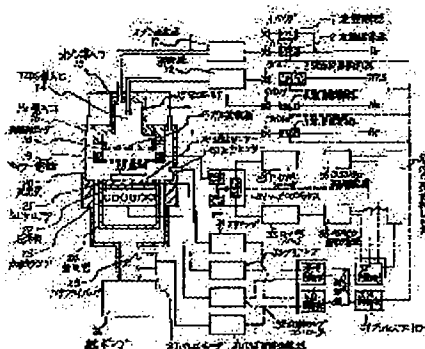
(72)Inventor : IKEDA YASURO

### (54) CHEMICAL VAPOR GROWTH, CHEMICAL VAPOR GROWTH DEVICE AND MANUFACTURE OF MULTILAYER WIRING

#### (57)Abstract:

**PURPOSE:** To decrease water content contained in a coating film and to prevent the generation of the defective connection of through holes, through which a lower layer aluminum wiring and an upper layer aluminum wiring are connected to each other, by a method wherein organic silane and oxygen are contained in raw gas and while the intensity of plasma emission on the surface of a substrate is periodically changed, a desired thin film is formed.

**CONSTITUTION:** The flow rate of liquid organic silane is adjusted by a liquid flow rate adjuster 3. The liquid organic silane is completely vaporized by an evaporator 12, mixed with helium flowing at a flow rate adjusted by a flow rate adjuster 4, and organic silane gas is produced. Ozone-containing gas is produced by introducing oxygen supplied at a flow rate adjusted by a flow rate adjuster 2 in a silent discharge ozone generator 11. The produced organic silane gas and ozone-containing oxygen gas are introduced in a manifold 15. When the outputs of high-frequency power supplies 35 and 36 are changed in synchronizaton with a pulse, which is generated by a pulse generator 40, plasma between a shower electrode 19 and a substrate 28 is periodically changed to form a desired thin film. Accordingly, the amount of water content in an interlayer film is decreased and the crack resistance is enhanced.



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(12) 公開特許公報(A)

(11)特許出願公開番号

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(43)公開日 平成6年(1994)6月14日

(51)Int.Cl. <sup>5</sup>	識別記号	庁内整理番号	F I	技術表示箇所
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C 2 3 C 16/50		7325-4K		
C 3 0 B 25/14		9040-4G		
25/16		9040-4G		
H 0 1 L 21/316	Y	7352-4M		

審査請求 有 請求項の数10(全 24 頁) 最終頁に続く

(21)出願番号 特願平4-320973

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(71)出願人 000004237

日本電気株式会社

東京都港区芝五丁目7番1号

(72)発明者 池田 康郎

東京都港区芝五丁目7番1号日本電気株式会社内

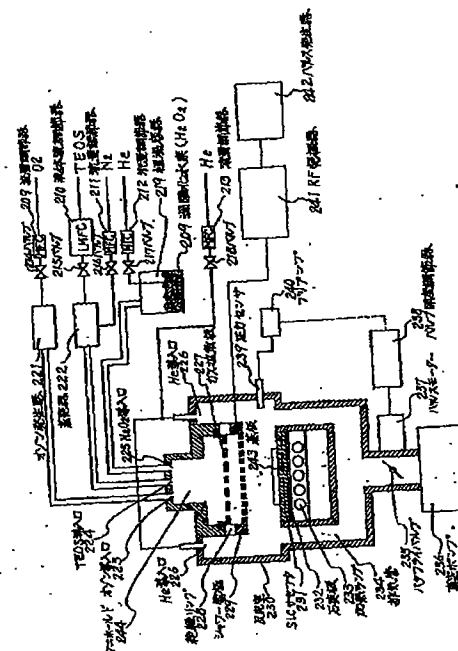
(74)代理人 弁理士 京本 直樹 (外2名)

(54)【発明の名称】 化学気相成長法と化学気相成長装置および多層配線の製造方法

(57)【要約】

【目的】段差被覆性が良く、アスペクト比が1.0以上のサブミクロン設計ルールのアルミ配線をボイド無く埋設でき、かつ、膜中水分が少なく、耐クラック性、耐ストレスマイグレーション性、スルーホール性、絶縁性に優れた多層配線層間膜用化学気相成長絶縁膜を提供し、工程数の低減による歩留り向上およびコスト低減と、多層配線の高信頼性化を達成する。

【構成】反応ガスとしてTEOSとオゾンと過酸化水素(H<sub>2</sub>O<sub>2</sub>)を用い、パルス発生器242から、周期1秒、デューティー30%のパルスを送り、RF発振器241からシャワー電極229に印加する高周波電力をオン・オフする事により、約2nmのTEOSとオゾンとH<sub>2</sub>O<sub>2</sub>の熱CVD膜の形成、熱CVD膜のプラズマ膜への改質、約5nmのプラズマTEOS・CVD膜の形成が繰り返される。これにより、プラズマTEOS・CVD膜と同等の膜質を持ち、段差被覆性、微細配線埋め込み性の優れた、層間絶縁膜が形成される。



## 【特許請求の範囲】

【請求項1】 原料ガスの少なくとも一部分に有機シランと酸素を含み、基板方面へのプラズマ照射強度を周期的に変化させながら所望の薄膜を形成する事を特徴とするプラズマ化学気相成長法。

【請求項2】 原料ガスの少なくとも一部分に有機シランとオゾン含有酸素を含み、基板表面へのプラズマ照射強度を周期的に変化させながら所望の薄膜を形成する事を特徴とする請求項1記載の化学気相成長法。

【請求項3】 前記プラズマ照射強度の周期的な変化を、プラズマの発生状態と非発生状態の繰り返しにより行う事を特徴とする請求項1または請求項2記載のプラズマ化学気相成長法。

【請求項4】 前記プラズマ照射強度の周期的な変化を、基板表面へのプラズマの照射および非照射の繰り返しにより行う事を特徴とする請求項1または請求項2記載のプラズマ化学気相成長法。

【請求項5】 ウェハ表面に有機シランおよび酸素を供給する機構と、酸素プラズマイオン源と、プラズマ照射強度を周期的に変化させるためのシャッターとを有する事を特徴とする化学気相成長装置。

【請求項6】 原料ガスとして有機シランと酸素あるいはオゾンとを用いる化学気相成長法であって、さらに過酸化水素 ( $\text{H}_2\text{O}_2$ )、水素 ( $\text{H}_2$ )、水 ( $\text{H}_2\text{O}$ )、炭化水素、アルコール、カルボニル化合物、カルボン酸の内の少なくとも1種類を添加する事を特徴とする化学気相成長法。

【請求項7】 プラズマを照射することを特徴とする請求項6記載の化学気相成長法。

【請求項8】 基板表面へのプラズマ照射強度を周期的に変化させながら所望の薄膜を形成する事を特徴とする請求項7記載の化学気相成長法。

【請求項9】 前記プラズマ照射強度の周期的な変化を、プラズマの発生状態と非発生状態の繰り返しにより行う事を特徴とする請求項9記載の化学気相成長法。

【請求項10】 原料ガスに有機シランと、オゾンあるいは酸素と、過酸化水素、水素、水、炭化水素、アルコール、カルボニル化合物、カルボン酸の内の少なくともひとつを添加し、金属配線に絶縁膜を金属配線の高さ以上の膜厚だけ形成する工程と、レジスト膜、有機シリカ膜等の平坦化膜を形成する工程と、反応性イオンエッチング法によりエッチバックする工程を含む事を特徴とする多層配線の製造方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は、化学気相成長法と化学気相成長装置および多層配線の製造方法に関する。

## 【0002】

【従来の技術】 従来のプラズマ化学気相成長法は、反応ガスにTEOS及び酸素を用い、反応容器内の対向電極

間に、一定出力の高周波電力を印加し、一定強度のプラズマを発生させながら、被処理基板上に所望の薄膜を形成していた。

【0003】 図9に、従来のプラズマ気相成長装置の概略図を示す。

【0004】 シリコン原料となるTEOS（テトラエチルオルソシリケート）ガスは、バブラー132に入れた液体状のTEOS131を、流量調節器123にて流量調節されたヘリウム（He）ガスにてバブリングし、TEOSを蒸発させて生成する。オゾン含有酸素は、流量調節器120で流量調節された酸素ガスをオゾン発生器165を通過させ、濃度10%程度のオゾンを含ませて生成する。TEOSガス及びオゾン含有酸素ガスは、TEOS導入口138及び酸素・オゾン導入口139よりマニホールド136に導入され、マニホールド136内で混合されて、ガス拡散板140に当たり拡散し、シャワー電極142を通過してさらに均一に分散し、基板147の表面に吹き付けられる。基板147は、SiCセクタ144上に装着され、石英板145を通して加熱ランプ146から光加熱され、350℃程度の温度に保持されている。シャワー電極142は、絶縁リング141によって他の部分と電気的に絶縁されており、13.56MHz高周波電源129およびハイパスフィルター130、450kHz高周波電源133およびローパスフィルター134で生成された2つの周波数の高周波電圧が、マッチングボックス135を介して印加されている。排気管148は真空ポンプ149に接続されており、反応室143の圧力は、数Torrに保持されている。

【0005】 通常、上記のような装置では、まず、TEOSガスと酸素の混合ガスをシャワー電極142から基板147に吹き付け、圧力等の安定を確認した後、一定の高周波電圧をシャワー電極142に印加し、TEOS及び酸素を分解させて基板147上に所望の膜を形成する。

【0006】 このような単純な方法では、形成された膜の下地段差に対する段差被覆性（ステップカバレッジ）が悪い（約50%）事が判っており、プラズマ化学気相成長法と、オゾンとTEOSの熱化学気相成長法とを交互に行うことが試みられている。図10に、そのような方法を行う際に、シャワー電極142に印加される高周波電力と、プラズマ中の酸素イオン数と、原料ガス中のオゾン濃度の、成膜時間に対する変化を示している。プラズマ化学気相成長を行っており、高周波電力が印加されている期間は、酸素イオン数が最大値を示すが、オゾン熱化学気相成長を行っており、高周波電力がゼロの期間は、酸素イオン数もゼロになっている。また、高周波電力をゼロにしてから、オゾンを流し始めるため、オゾン濃度が上昇するまでに一定時間が必要である。上記のように、プラズマ化学気相成長法とオゾン熱化学気相

成長法を交互に行なった場合、膜がどのように形成されるかを、図11(a)～(d)に示す。下地基板上に形成されたアルミ配線153上に、まず(b)の様に、プラズマCVD膜154が形成される。次に、(c)の様に、アルミ配線間の狭いスペースを埋め込むために、第1の熱CVD膜155が形成される。さらに、(d)の様に、第2のプラズマCVD膜156が形成される。このような工程が繰り返されて所望の膜厚まで膜形成が行われ、図11(d)の様に、多層構造の膜が形成される。特に、このような方法では、オゾン熱CVD膜155がそのままの形で残っている事が重要である。なぜならば、オゾン熱CVD膜155の成膜条件が適正でないと膜中に水分が多く残存し、アルミ配線の層間接続孔から水蒸気が噴出したり、水蒸気によって層間膜の剥離が生じたり、アルミ配線の層間接続孔での接続不良(スルーホール不良)が発生したりという問題が生じる。これらの問題に対して、オゾン熱CVD膜155の成膜を高オゾン濃度条件で行うことが有効であることが知られている。しかし、そのような高オゾン濃度条件下では、第1のプラズマCVD膜154上でのオゾン熱CVD膜155のステップカバレッジが劣化することも知られている。これは、第1のプラズマCVD膜154の膜質が、アルミ配線153の上面と側面と異なるために起こると考えられている。

【0007】図12は、従来のプラズマ化学気相成長法とシリカ塗布法を用いた、多層配線用平坦化絶縁膜の形成方法を示している。まず、図12(a)、(b)の様に、基板157上に形成されたアルミ配線158の上に、プラズマCVD膜159を、配線間スペースに鬆(ボイド)ができない程度の厚さだけ形成する。次に、図12(c)の様にシリカ塗布液を塗布し、溶剤蒸発の為に100℃の熱処理、膜質改善の為に300℃前後の熱処理を行い、シリカ塗布膜(1回塗布)160を形成する。このままでは、平坦性が不十分なので、図12(d)の様に、図12(c)で行なったシリカ塗布及び熱処理の工程を、2回以上繰り返して、シリカ塗布膜(複数回塗布)161を形成する。さらに、通常の反応性イオンエッチング法(RIE)を用いてエッチバックする。この時、アルミ配線上のプラズマCVD酸化膜が露出すると、酸化膜から酸素原子が供給されるため、シリカ塗布膜のエッチングレートが大きくなり、図12(e)の様に、エッチバック後のシリカ塗布膜162は、アルミ配線段差間のスペース部がへこんでしまう事が知られている。最後に、再度、プラズマCVD膜163を形成して層間膜が完成する。

【0008】

【発明が解決しようとする課題】上述の従来のプラズマ化学気相成長法は、段差被覆性(ステップカバレッジ)が悪く、サブミクロンのアルミ配線間スペースを埋設する事ができなかった。サブミクロンのアルミ配線間ス

ペースを埋設する為には、図11のように、プラズマ化学気相成長法と、オゾンとTEOSの熱化学気相成長法とを交互に行ったり、図12の様に、シリカ塗布膜を多数回形成する必要がある。しかし、10 Torr程度の減圧下で形成されたオゾン-TEOS熱CVD膜やシリカ塗布膜は、膜中に含まれる水分が多く、機能的強度、絶縁特性等に問題があり、特に、下層アルミ配線と上層アルミ配線を接続するスルーホールの接続不良が生じるという欠点があった。また、高オゾン濃度条件で成膜すると膜中水分は減少するが、ステップカバレッジが劣化し、完全な埋め込みが出来なくなる不具合があった。さらにまた、図12のようなシリカ塗布膜をエッチバックする方法では、シリカ塗布膜を形成する工程や、エッチバックする工程が非常に複雑で、工程数の増加や、歩留まり低下を招くという欠点も有った。

【0009】

【課題を解決するための手段】本発明の化学気相成長法は、原料ガスとして、有機シランと、酸素あるいはオゾンとを含み、さらに過酸化水素(H<sub>2</sub>O<sub>2</sub>)、水素(H<sub>2</sub>)、水(H<sub>2</sub>O)、炭化水素、アルコール、カルボニル化合物、カルボン酸の内の少なくとも1種類を含んでいる。また、本発明のプラズマ化学気相成長法は、原料ガスの少なくとも一部分に有機シランと酸素あるいはオゾン含有酸素を含み、基板表面へのプラズマ照射強度を周期的に変化させながら所望の膜を形成する。この際、プラズマ照射強度を変化させる手段として、プラズマの発生状態と非発生状態を繰り返して行ったり、基板表面へのプラズマの照射および非照射を繰り返したり、反応容器内の対向する電極に、2種以上の周波数の高周波電圧を印加し、その内の一部あるいは全部の高周波電力を周期的に変化させる。

【0010】また、本発明の化学気相成長装置は、有機シランを供給する機構と、オゾン含有酸素を供給する機構と、過酸化水素、水素、水、炭化水素、アルコール、カルボニル化合物、カルボン酸の内の少なくとも1種類をガス状態にして供給する機構とを有している。また、本発明の化学気相成長装置は、有機シランを供給する機構と、酸素あるいはオゾン含有酸素を供給する機構と、プラズマ発生強度を周期的に変化させる機構、或いは、1つの反応容器内に設けられたプラズマ強度の異なる複数のプラズマ照射機構と、この複数のプラズマ照射機構の間で基板を移動させる機構とを有している。さらに、本発明の化学気相成長装置は、ウェハ表面に有機シランおよびオゾン含有酸素を供給する機構と、酸素プラズマイオン源と、プラズマ照射強度を周期的に変化させるための機械的或いは電磁的なシャッターとを有している。また、本発明の化学気相成長装置は、反応容器内の対向する電極に、2種以上の周波数の高周波電圧を印加し、その内の一部あるいは全部の高周波電力を周期的に変化させる機構を有している。

【0011】さらに、本発明の多層配線の製造方法は、原料ガスに有機シランと、オゾンあるいは酸素を含み、さらに、過酸化水素、水素、水、炭化水素、アルコール、カルボニル化合物、カルボン酸の内の少なくともひとつを添加する化学気相成長法により、金属配線上に絶縁膜を金属配線の高さ以上の膜厚だけ形成する工程と、レジスト膜、有機シリカ膜等の平坦化膜を形成する工程と、反応性イオンエッチング法によりエッチバックする工程を含んでいる。また、本発明の多層配線の製造方法は、有機シランとオゾンあるいは酸素を原料ガスとし、基板表面へのプラズマ照射強度を周期的に変化させ金属配線上に絶縁膜を金属配線の高さ以上の膜厚だけ形成する工程と、レジスト膜、有機シリカ膜等の平坦化膜を形成する工程と、反応性イオンエッチング法によりエッチバックする工程を含んでいる。

【0012】

【実施例】次に、本発明について、図面を参照して説明する。

【0013】図1は、本発明の第1の実施例を表すプラズマ化学気相成長装置の概略縦断面図であり、図2は、図1のプラズマ化学気相成長装置の動作を、印加高周波電力、酸素イオン数、オゾン濃度の時間変化について表したものであり、図3は、本発明の原理の概略を表すモデル図であり、図4は、図2のような動作を行った際の、時間経過と膜の成長過程を表す縦断面図であり、図5は、図2のような動作を行った際、高周波オン時間( $t_{ON}$ )の割合(デューティD)と膜成長速度、ステップカバレージ、OH基の吸収係数の関係を示す。

【0014】図1は、本発明の実施例1のプラズマ化学気相成長装置の概略縦断面図である。本実施例の装置では、シリコン原料となる珪酸エチル(以下TEOSと呼ぶ)ガスは、この図では表されていないTEOSタンクから供給される、液体状のTEOSを、マスフロー型の液体流量調節器3で流量調節し、蒸発期12で完全に気化させ、流量調節器4で流量調節されたヘリウムと混合されて生成される。オゾン含有酸素は、流量調節器2で流量調節された酸素を、無声放電型オゾン発生器11に導入し、1~10%のオゾン含有させて生成される。このようにして生成された、TEOSガス及びオゾン含有酸素ガスは、TEOS導入口14及びオゾン導入口13からマニホールド15に導入される。マニホールド内では、これらのガスは混合され、ガス拡散板17に当たる事によって、ほぼ均一に拡散する。さらに、シャワー電極19に当たると、さらに均一に分散し、基板28の表面に吹き付けられる。基板28は、SiCサセプタ21上に装着され、石英板22を通して加熱ランプ23から光加熱され、200~450℃程度の温度に保持されている。シャワー電極19は、絶縁リング18によって他の部分と電気的に絶縁されており、13.56MHz高周波電源39およびハイパスフィルター38、450

kHz高周波で源36およびローパスフィルター35で生成された2つの周波数の高周波電圧が、マッチングボックス37を介して印加されている。排気管24は真空ポンプ26に接続されており、反応室20の圧力は、0.1~数十Torrに保持されている。

【0015】本実施例では、シャワー電極19に接続されているマッチングボックス37の内部に、2つの周波数の高周波電圧を混合する混合器部と、インピーダンス整合を行うマッチング部と、ダミーロードと、半導体スイッチがあり、シャワー電極19に印加する高周波電圧をオン・オフ出来るようになっている。また、パルスジェネレータ40の発生するパルスに同期して、高周波電源35、36の出力を変化させ、シャワー電極19に印加される高周波電圧を変化させる事も可能である。これらの動作は、基板温度、反応室圧力等も含めて、プロセスコントローラー41で制御される。これらの制御信号やパルス等の伝達路は、図1中では破線で示されている。

【0016】ここで、シャワー電極19に印加する高周波電圧を、周期1秒でオン・オフした場合の本装置の動作を、図2、図3、図4及び、図5を用いて説明する。

【0017】図2最下断は、成膜時間と高周波電力の関係を示している。高周波電力がオンになっている時間 $t_{ON}$ の間、シャワー電極19と基板28或いはSiCサセプタ21の間にプラズマが発生し、酸素或いはオゾンが分解し酸素イオンが発生する。図2中段は、その酸素イオン数の変化を表している。高周波電力を印加し始めてからプラズマ状態が安定するまでには、ある一定の時間が必要で、なで肩の波形になっている。オゾンは酸素より不安定であるため、高周波電力の印加によるイオン化効率は高い。そのため、プラズマ中のオゾン分子数は、図2上段のように、高周波電力がオンの時、かなり低下する。

【0018】図3(a)、(b)は、それぞれ、高周波オンおよびオフの時の基板表面近傍の様子を表すモデル図である。高周波オンの時、図1のシャワー電極19と基板28の間にプラズマが発生する。プラズマ中では、酸素分子やTEOS分子は、電子45、酸素イオン47、TEOS解離分子46、酸素ラジカル55等に解離する。また、プラズマと基板の間には、シース電圧が発生し、酸素イオン47は、この電圧により加速され、ドリフトし、基板表面に衝突する。TEOS解離分子46も基板表面に向かって拡散し、形成膜表面で、熱分解或いは酸素イオン衝撃による分解によって膜形成前駆体50になる。さらに、形成膜表面で酸素ラジカル等と反応し、形成膜51が形成される。この際、形成膜51の表面には、非常に多くの酸素イオン衝撃があるため、膜形成前駆体50の寿命はかなり短く、形成膜表面での密度は低い。また、酸素イオン衝撃は、形成膜51を硬化させる作用があり、膜質が良好で、圧縮応力の膜の形成

に役立っている。

【0019】さて、一旦高周波がオフになると（図3（b）参照）、電子および酸素イオン数は速やかに減少するが、TEOS解離分子46や酸素ラジカル55は、なおも残っている。これらは、形成膜51の表面に拡散して膜形成前駆体50となりやがて減少する。さらに、TEOS分子54とオゾン分子56も膜表面に向かって拡散し、反応してTEOS解離分子や膜形成前駆体となる。形成膜51の表面では、膜形成反応が熱化学反応のみであるため、形成膜表面に、膜形成前駆体が高密度で存在し、膜形成前駆体凝液体層59が形成される。この膜形成前駆体凝液体層59は、液体の性質を示すため、基板52に形成されている段差の側面低部の膜厚が厚くなり、段差側面の傾きを緩和する。

【0020】図4は、図2のように高周波電力を印加したときの時間経過と膜形成の様子をモデル的に示した縦断面図である。まず、図4（a）のように、時間 $t_{ON}$ （図2では0.5秒）の間、高周波がオンになり、約10nmの第1のプラズマCVD膜60が形成される。次に、図4（b）の様に、時間 $t_{OFF}$ （0.5秒）の間第1の熱CVD膜62が形成される。時間 $t_{OFF}$ は0.5秒と非常に短く、第1の熱CVD膜62の膜厚は1nm程度である。そのため、次の $t_{ON}$ の初期に酸素イオン衝撃等で改質され、プラズマCVD膜と同等の膜質になってしまう。よって、図4（c）のように、改質された第1の熱CVD膜62は、第1のプラズマCVD膜60と区別がつかなくなってしまう。第1のプラズマCVD膜60に取り込まれてしまう。熱CVD膜は、膜形成前駆体凝液体層の効果で、配線間の狭小なスペースや段差低部の角を埋め込み、形状をスムーズにする事が出来るので、続くプラズマCVD膜成長初期のプラズマ照射により、熱CVDと同等の形状でプラズマCVDと同等の膜質の第2プラズマCVD膜成長前の形成膜64を形成した事になる。第2プラズマCVD膜成長前の形成膜64により、段差低部は丸みを帯びた形状になっているため、この上に形成される第2のプラズマCVD膜63の形状も、図4（c）の様に、丸みを帯びる。第2プラズマCVD膜成長前の形成膜64と第2のプラズマCVD膜63も区別がつかないため、続く第2の熱CVD膜65の成長段階（d）では、下層膜は第2プラズマCVD膜成長後の形成膜66になる。

【0021】以上のような段階を、多数回繰り返すことにより、図4（e）のように、アルミ配線61の間のスペース部に鬆（ポイド）無く、プラズマCVD膜とほぼ同等の、良好な膜質の形成膜を埋め込む事が出来る。

【0022】図5は、図2中の $t_{ON}$ と $t_{OFF}$ から計算されるデューティー比D（ $D = t_{ON} / (t_{ON} + t_{OFF}) \times 100 (\%)$ ）の値と、成長速度、ステップカバレッジ、膜中のOH基の吸収係数との関係を示している。図5最下段から、成長速度はDが大きいほど増加する事が

判り、中断から、ステップカバレッジは、Dが50%を超えると悪化し始める事が判り、上段から、OH基は、Dが40%を超えれば十分小さくなる事が判る。図4から、ステップカバレッジと膜中水分量（膜中OH基吸収係数）は相反する傾向にあるが、デューティー比Dの値を適当な範囲（本実施例の場合は40から60パーセント）に設定することにより両者とも損なわないようにする事が出来る事が判る。

【0023】尚、本実施例では、有機シランガスとして、珪酸エチル（TEOS：化学式 $Si(OC_2H_5)_4$ ）を用いたが、テトラメチルシラン（TMS：化学式 $Si(CH_3)_4$ ）、テトラメチルシクロテトラシロキサン（TMCTS）、オクタメチルシクロテトラシロキサン（OMCTS）、ヘキサメチルジシラザン（HMDs）、トリエトキシシラン（ $SiH(OC_2H_5)_3$ ）、トリシメチルアミノシラン（ $SiH(N(CH_3)_2)_3$ ）等のシリコン含有化合物を用いても同様の結果が得られる。

【0024】また、反応ガス中のオゾンが存在しなくても、酸素ラジカルやTEOS解離分子の寿命はかなり長いので、デューティー比の値を適当に選べば、同様の結果が得られる。さらに、反応ガス中に、シラン等のシリコン無機化合物やアンモニア等窒素化合物や、リン、ホウ素、砒素、アンチモン等の水素化合物や有機化合物を混入させた場合にも同様の結果が得られる。

【0025】さらにまた、本実施例では、シャワー電極19に印加する高周波電力のみを変化させたが、パルスジェネレータ40の生成するパルスに同期して、高周波電力、反応室圧力、基板温度、ガス流量等を変化させると、より良好な段差被覆性が得られる。

【0026】図6（a）は、本発明の第2の実施例のプラズマ化学気相成長装置の反応室の概略平面図であり、図6（b）は、図6（a）のA-A'線に沿った縦断面図である。尚、図6（a）は、図6（b）のB-B'線に沿った平面図を表している。

【0027】反応室72は、6つの扇型の領域に分けられ、時計の3時の方向の扇型が熱CVD領域70になっており、時計回りに、プラズマCVD領域、熱CVD領域、プラズマCVD領域166と交互に配置されている。基板69は、回転軸79を軸として回転するサセプター71の上に装着され、熱CVD領域と、プラズマCVD領域を交互に通過するようになっている。

【0028】熱CVD領域70には、TEOS導入口73とオゾン導入口75から、TEOSガス及びオゾン含有酸素が導入され、ガス分散板83とシャワーインジェクター81で均一に分散された後、基板69の表面へ供給される。基板69はサセプター71の裏側に設置されたヒーター80によって約350℃に加熱されているため、基板上でオゾンとTEOSによる熱CVD膜が成長する。



【0029】プラズマCVD領域166には、TEOS導入口73と酸素導入口74からTEOSガス及び酸素ガスが導入され、ガス分散板83'とシャワー電極78で均一に分散され、基板69'の表面に供給される。シャワー電極78は、絶縁リング82及び絶縁体76によって、反応室の他の部分から電気的に絶縁されており、RF導入端子77から13.56MHz或いは450kHzの高周波電圧が印加される。これらの高周波電圧の印加によって、シャワー電極78と基板69'或いは、サセプター71の間にプラズマが励起され、プラズマCVD膜が形成される。

【0030】前述したように、基板69は、回転するサセプター71とともに、プラズマCVD領域と熱CVD領域を交互に通過するため、プラズマCVD膜と熱CVD膜が交互に形成される。この際、サセプター71の回転速度を毎分10回転程度にすると、熱CVD領域70で形成される熱CVD膜の膜厚は約2nm程度となり、隣合うプラズマCVD領域の成膜初期でプラズマ照射され、膜質はプラズマCVD膜と同様になる。このようにして、図4で述べたのと同様に膜質はプラズマCVD膜と同様で、ステップカバレッジ及び段差埋め込み性に優れたCVD膜が形成される。

【0031】尚、本実施例では、反応室を6つの領域に分割したが、これは2つ以上であれば幾つでも構わない。また、成膜領域の種類を熱CVD領域とプラズマCVD領域の2種類にしたが、プラズマCVD領域を印加する高周波の周波数や印加電力によって2種以上設けても良い。

【0032】さらに、本実施例では、サセプター71を平面のターンテーブル状にし、上方に、シャワーインジェクターやシャワー電極を設けたが、サセプターを円筒或いは多角柱状にし、その外側面に基板を装着し、基板と対向してシャワー電極等を設けても同様の結果が得られる。

【0033】また、本実施例では、有機シランガスとして、珪酸エチル(TEOS:化学式 $\text{Si}(\text{OC}_2\text{H}_5)_4$ )を用いたが、テトラメチルシラン(TMS:化学式 $\text{Si}(\text{CH}_3)_4$ )、テトラメチルシクロテトラシロキサン(TMCTS)、オクタメチルシクロテトラシロキサン(OMCTS)、ヘキサメチルジシラザン(HMDS)、トリエトキシシラン(化学式 $\text{Si}(\text{OC}_2\text{H}_5)_3$ )、トリスジメチルアミノシラン(化学式 $\text{Si}(\text{H}(\text{N}(\text{CH}_3)_2)_3$ )等のシリコン含有化合物を用いても同様の結果が得られる。

【0034】また、反応ガス中にオゾンが存在しなくても、酸素ラジカルやTEOS解離分子の寿命はかなり長いので、デューティー比の値を適当に選べば、同様の結果が得られる。さらに、反応ガス中に、シラン等のシリコン無機化合物やアンモニア等窒素化合物や、リン、ホウ素、砒素、アンチモン等の水素化合物や有機化合物を混

入させた場合にも同様の結果が得られる。

【0035】図7は、本発明の第3の実施例のプラズマ化学気相成長装置の概略を表す縦断面図である。

【0036】イオン源空洞93には、流量調節器103で流量調節された酸素ガス $\text{O}_2$ と、流量調節器87で流量調節されたアルゴンガスArが供給され、圧力は、 $p=1\text{mTorr}$ に保たれている。また、マイクロ波電源84から、導波管85及び透過窓86を経由して、周波数2.54GHzのマイクロ波が供給されている。さらに、主電磁石コイル94の作る875ガウスの磁場によって、イオン源空洞93内では電子サイクロトロン共鳴(ECR)が起こっており、イオン化率の高い酸素プラズマが発生する。酸素イオンは主電磁石コイル94の発散磁界及び補助コイル96によって反応室95へ引き出され、基板106へ照射される。シリコン原料となるTEOSガスは、80°Cに保たれた恒温容器112内に保温されたTEOS111から蒸発したTEOSガスを、流量調節器113で流量調節してTEOS導入口107から反応室へ導入される。また、流動調節器101で流量調節された酸素ガスが、オゾン発生器98を通過してオゾン含有酸素になり、オゾン導入口97から供給される。基板106は、サセプター109上に装着され、ヒーター110によって300°Cに加熱されている。また、反応室の圧力は、流量調節器88によって流量調節され、Ar導入口108から供給される希釈用アルゴンガスと真空ポンプ105によって、約1mTorrに保たれている。

【0037】本実施例のプラズマCVD装置では、まず、イオン源空洞93内に酸素プラズマを発生させる。補助コイル96、96'に流す電流は、イオン源から基板に向かう磁場を発生させる向きで小さな値にしておき、酸素プラズマの照射が均一になる程度にしておく。また、反射磁石コイル102、102'に流す電流も、イオン源から基板に向かう磁場を発生させる向きで小さな値にしておく。この状態で、基板106表面に酸素イオンを照射させ、TEOSガスを供給すると、ECRプラズマ気相成長が起こり、膜質の良いプラズマCVD膜が形成される。を約10nm形成する。次に、補助コイル96、96'に流す電流の値を強くして、イオン源空洞出口付近にミラー型磁場が形成されるようにし、主電磁石コイル94、94'の発散磁界によってプラズマから流れ出す電子及びイオンが跳ね返るようにする。すると、基板106上には、TEOSガスとイオン源から拡散してくる酸素ラジカル、酸素分子等の中性粒子のみが供給され、熱CVD的な反応のみが起こり、ステップカバレッジの良い成膜が行われる。そこで、補助コイル96、96'に流す電流を1秒から10秒程度の周期で変化させると、基板106に照射される酸素イオン数が周期的に変化し、プラズマCVD膜と熱CVD膜が交互に形成され、さらに、熱CVD膜のプラズマCVD膜への

改質も行われて、図4と同様に、ステップカバレッジ及び段差埋め込み性に優れたプラズマCVDが形成される。特に本実施例では、反応室圧力を1mTorr程度にしているので、アスペクト比の大きな溝の受け込みも可能になる。

【0038】尚、基板106に照射される酸素イオンを変化させる手段として、上記の例では補助コイル94によって形成されるミラー型磁場を用いたが、反射磁石102、102'によって形成されるカスプ型磁場や、セプター109に正の電圧を印加して形成される反跳電場を用いても良い。また、図7には示されていないが、機会的なシャッターを用いても同様の結果が得られる。但し、機械的シャッター等を用いて、酸素ラジカルの拡散を妨げるような構造にした場合には、オゾン発生器98を動作させて基板近傍にオゾンを供給し、熱化学気相成長を促進し、熱CVD膜の成長を促進するようにした方がよいのは言うまでもない。

【0039】また、上記実施例では、イオン源として電子サイクロトロン共鳴型(ECR)イオン源を用いたが、酸素イオンの強度を変化させる事が出来れば、その形式によらず同様の結果が得られる。

【0040】また、本実施例では、有機シランガスとして、珪酸エチル(TEOS:化学式 $\text{Si}(\text{OC}_2\text{H}_5)_4$ )を用いたが、テトラメチルシラン(TMS:化学式 $\text{Si}(\text{CH}_3)_4$ )、テトラメチルシクロテトラシロキサン(TMCTS)、オクタメチルシクロテトラシロキサン(OMCTS)、ヘキサメチルジシラザン(HMDS)、トリエトキシシラン(化学式 $\text{Si}(\text{OC}_2\text{H}_5)_3$ )、トリスジメチルアミノシラン(化学式 $\text{Si}(\text{H}(\text{N}(\text{CH}_3)_2)_3$ )等のシリコン含有化合物を用いても同様の結果が得られる。

【0041】さらに、反応ガス中に、シラン等のシリコン無機化合物やアンモニア等窒素化合物や、リン、ホウ素、砒素、アンチモン等の水素化合物や有機化合物を混入させた場合にも同様の結果が得られる。

【0042】図8は、本発明の第4のアルミ多層配線の層間絶縁膜平坦化法を表す縦断面図である。

【0043】本実施例では、まず、半導体素子等を形成した基板115上にアルミ配線114を形成する(図8(a))。次に、本発明の実施例1のプラズマ化学気相成長装置を用いて、図中(b)、(c)のように、本発明のCVD膜116をアルミ配線の膜厚より厚く形成する。レジスト117を塗布しハードベークする。レジスト117と本発明のCVD膜116のエッチングレートが等しくなるように調整した反応性イオンエッチング法を用いて、エッチバックを行い、CVD膜の表面が平坦になるようにする。すると、平坦化された層間膜118が出来上がる。

【0044】尚、本実施例では、平坦化のためにレジストを用いたが、ポリエチレンや有機SOG等を用いても

同等の結果が得られる。また、平坦化法として、研磨法を用いれば、基板全面に渡って良好な平坦性が得られる。

【0045】図13は、図1の実施例1のプラズマ化学気相成長装置を使用した、第5の実施例の動作の方法を示している。図13では、13.56MHz高周波電力、450kHz高周波電力、イオン電流密度、平均イオンエネルギーについて表している。但し、いずれの値も、それぞれの値の最大値で規格化してある。

【0046】本実施例の動作の方法では、図13の下から1段目及び2段目の様に、図1の13.56MHzと450kHzの2つの周波数の高周波電源39、36に、パルスジェネレータ40からパルスを送り、2つの周波数の高周波の最大出力が逆位相になるようにして、シャワー電極19に電圧を印加している。すると、図13下から3段目および4段目の様に、イオン電流密度の変化は小さいが、平均イオンエネルギーは、450kHz高周波電力が最大の時に最大値を取り、13.56MHz高周波電力が最大の時に最小となるように出来る。これは、印加する高周波の周波数が高いと、プラズマと基板の間に生ずる電圧(シース電圧)が減少する事による。このように、イオン電流密度を変えないで、イオンエネルギーのみを変化させた場合、イオン衝撃の強度は周期的に変化し、膜質の劣化が無く、段差被覆性および溝埋め込み性が改善される点では、実施例1と同様であるが、さらに、図13最上段の様に、膜成長速度の変化が10%程度に小さくできるという利点がある。

【0047】尚、本実施例では、図1の装置を用いたが、本発明の他の実施例で示した、図6、図7の装置を用いても同様の結果を得る事が出来る。

【0048】尚、本実施例では、有機シランガスとして、珪酸エチル(TEOS:化学式 $\text{Si}(\text{OC}_2\text{H}_5)_4$ )を用いたが、テトラメチルシラン(TMS:化学式 $\text{Si}(\text{CH}_3)_4$ )、テトラメチルシクロテトラシロキサン(TMCTS)、オクタメチルシクロテトラシロキサン(OMCTS)、ヘキサメチルジシラザン(HMDS)、トリエトキシシラン(化学式 $\text{Si}(\text{OC}_2\text{H}_5)_3$ )、トリスジメチルアミノシラン(化学式 $\text{Si}(\text{H}(\text{N}(\text{CH}_3)_2)_3$ )等のシリコン含有化合物を用いても同様の結果が得られる。

【0049】また、反応ガス中にオゾンが存在しなくても、酸素ラジカルやTEOS解離分子の寿命はかなり長いので、デューティー比の値を適当に選べば、同様の結果が得られる。さらに、反応ガス中に、シラン等のシリコン無機化合物やアンモニア等窒素化合物や、リン、ホウ素、砒素、アンチモン等の水素化合物や有機化合物を混入させた場合にも同様の結果が得られる。

【0050】さらにまた、本実施例では、シャワー電極19に印加する高周波電力のみを変化させたが、パルスジェネレータ40の生成するパルスに同期して、高周波

電力、反応室圧力、基板温度、ガス流量等を変化させると、より良好な段差被覆性が得られる。

【0051】図14は、本発明の第6の実施例のプラズマ化学気相成長装置の概略縦断面図である。本実施例の装置では、シリコン原料となる珪酸エチル（以下TEOSと呼ぶ）ガスは、この図では表されていないTEOSタンクから供給される液体状のTEOSを、マスフロー型の液体流量調節器175で流量調節し、蒸発器187で完全に気化させ、流量調節器176で流量調節されたヘリウムと混合されて生成される。オゾン含有酸素は、流量調節器174で流量調節された酸素を、無声放電型のオゾン発生器186に導入し、1～10%のオゾンを含ませて生成される。また、過酸化水素ガスは、恒温容器177内の液体過酸化水素185を流量調節器177で流量調節されたヘリウムでバブリングすることにより生成される。過酸化水素ガスの濃度は、恒温容器184の温度で調節されるが、本実施例では10～20℃の範囲で使用した。このようにして生成された、TEOSガス、オゾン含有酸素ガスおよび過酸化水素ガスは、TEOS導入口189、オゾン導入口188および酸化水素ガス導入口190からマニホールド208に導入される。マニホールド内では、これらのガスは混合され、ガス拡散板192に当たる事によって、ほぼ均一に拡散する。さらに、シャワー電極194に当たると、さらに均一に分散し、基板207の表面に吹き付けられる。基板207は、SiCサセプタ196上に装着され、石英板197を通して加熱ランプ198から光加熱され、200～450℃程度の温度に保持されている。シャワー電極194は、絶縁リング193によって他の部分と電気的に絶縁されており、RF発振器206で発生される13.56MHzの高周波が印加されている。排気管199は真空ポンプ201に接続されており、反応室195の圧力は、0.1～数十Torrに保持されている。

【0052】本実施例では、以上の様な装置を用いて、成膜温度200℃、成膜圧力10Torr、RFパワー100W、TEOS流量50SCCM、酸素(O<sub>2</sub>)流量1SLM、オゾン濃度5%、過酸化水素(H<sub>2</sub>O<sub>2</sub>)流量0～5SCCMの成膜条件で絶縁膜を形成した。図16は種々の方法で形成した絶縁膜の、アルミ配線245上の縦断面形状を比較した図である。図16(a)は、従来のTEOSと酸素(O<sub>2</sub>)のプラズマ気相成長法を用いた絶縁膜（以下TEOS/O<sub>2</sub>系プラズマCVD膜と言う）、図16(b)は、本実施例の条件の内、過酸化水素(H<sub>2</sub>O<sub>2</sub>)流量が0SCCMの場合（つまり、オゾン含有酸素のみを用いた場合）。図16(c)は、本実施例の条件の内、過酸化水素(H<sub>2</sub>O<sub>2</sub>)流量が5SCCMの場合を示している。図16(a)と

(b)から、酸素の代わりにオゾン含有酸素を用いることにより、ステップカバレージがかなり改善されたことが判るが、アスペクト比が1.0を超えるスペースに於

いては、ポイド（鬆）249が生じることも判る。図16(c)から、オゾン含有酸素に加えてさらに過酸化水素ガス(H<sub>2</sub>O<sub>2</sub>)を添加することによって、アスペクト比が1.0を超えるスペースにおいてもポイド（鬆）の発生が無くなり、孤立アルミ配線の部分でもややフロア形状が形成されたことが判る。これらの結果は、添加された過酸化水素が、式(1)の様な化学式に従い分解し、



10 酸素ラジカル(・O)と水(H<sub>2</sub>O)を生成し、これらがTEOSの重合を促進するため、図3で示した膜形成前駆体50の生成が促進され、高周波電力を印加されプラズマが照射されている状態でも膜形成前駆体凝液体層59は形成されるためであると考えられる。

【0053】尚、本実施例では、添加ガスとして過酸化水素を用いたが、水素(H<sub>2</sub>)、水(H<sub>2</sub>O)、炭化水素、アルコール、カルボニル化合物、カルボン酸等のように酸素と反応して水(H<sub>2</sub>O)を生成する化合物を用いた場合、効果に差があるものの、同様の結果が得られた。また、過酸化水素を用いた場合、RF出力がゼロの場合も、過酸化水素を用いない場合に比べてフロー性の改善が認められた。また、本実施例では、有機シランガスとして、珪酸エチル(TEOS：化学式Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>)を用いたが、テトラメチルシラン(TMS：化学式Si(CH<sub>3</sub>)<sub>4</sub>)、テトラメチルシクロテトラシロキサン(TMCTS)、オクタメチルシクロテトラシロキサン(OMCTS)、ヘキサメチルジシラザン(HMDS)、トリエトキシシラン(化学式SiH(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)、トリスジメチルアミノシラン(化学式SiH(N(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>)等のシリコン含有化合物を用いても同様の結果が得られる。

【0054】図15は、本発明の第7の実施例のプラズマ化学気相成長装置の概略縦断面図である。本実施例の装置では、シリコン原料となる珪酸エチル（以下TEOSと呼ぶ）ガスは、この図では表されていないTEOSタンクから供給される、液体上のTEOSを、マスフロー型の液体流量調節器210で流量調節し、蒸発器222で完全に気化させ、流量調節器211で流量調節された窒素ガスと混合されて生成される。オゾン含有酸素は、流量調節器209で流量調節された酸素ガスを無声放電型のオゾン発生器221に導入し、1～10%のオゾンを含ませて生成される。また、過酸化水素ガスは、恒温容器219内の液体過酸化水素220を流量調整器212で流量調節されたヘリウムでバブリングすることにより生成される。過酸化水素ガスの濃度は、恒温容器219の温度で調節されるが、本実施例では10～20℃の範囲で使用した。このようにして生成された、TEOSガス、オゾン含有酸素ガスおよび過酸化水素ガスは、TEOS導入口224、オゾン導入口223および過酸化水素ガス導入口225からマニホールド244

に導入される。マニホールド内では、これらのガスは混合され、ガス拡散板227に当たる事によって、ほぼ均一に拡散する。さらに、シャワー電極229に当たると、さらに均一に分散し、基板243の表面に吹き付けられる。基板243は、SiCサセプタ231上に装着され、石英板232を通して加熱ランプ233から光加熱され、200~450℃程度の温度に保持されている。排気管234は真空ポンプ236に接続されており、反応室230の内部の圧力は、0.1~数十Torrに保持されている。シャワー電極229は、絶縁リング228によって他の部分と電気的に絶縁されており、RF発振器241で発生される13.56MHzの高周波が印加されている。このRF発振器241の出力は、パルス発生器242で発生されるパルスによって制御されており、周期的にON・OFFしたり、強度が変化したりする。

【0055】本実施例では、以上の様な装置を用いて、成膜温度350℃、成膜圧力10Torr、RF周波数13.56MHz、RFパワー100W、パルス周波数1Hz、デューティー比D=30%、TEOS流量50SCCM、酸素(O<sub>2</sub>)流量1SLM、オゾン濃度5%、過酸化水素(H<sub>2</sub>O<sub>2</sub>)流量0~5SCCMの成膜条件で絶縁膜を形成した。図17は本実施例の成膜条件で形成した絶縁膜の、アルミ配線251上の縦断面形状を示している。図から、本実施例によれば、アスペクト比が1.0を越えるスペース部を埋め込むだけでなく、フロー形状が得られ、滑らかな表面状態を有する絶縁膜が得られることが判る。

【0056】尚、本実施例では、RF発振器の周波数として13.56MHzを用いたが、本発明の実施例1と同様に、450Hz等の低周波を加えるとさらに良い結果が得られる。また、本実施例では、パルス発生器を用いてRFパワーのON・OFFを行ったが、図6の様な装置を用いて、プラズマの照射・非照射の状態を繰り返しても同様の結果が得られる。また、本実施例では、有機シランガスとして、珪酸エチル(TEOS:化学式Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>)を用いたが、テトラメチルシラン(TMS:化学式Si(CH<sub>3</sub>)<sub>4</sub>)、テトラメチルシクロテトラシロキサン(TMCTS)、オクタメチルシクロテトラシロキサン(OMCTS)、ヘキサメチルジシラザン(HMDS)、トリエトキシシラン(化学式SiH(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)、トリスジメチルアミノシラン(化学式SiH(N(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>)等のシリコン含有化合物を用いても同様の結果が得られる。

【0057】図18は、本発明の第8の実施例のプラズマ化学気相成長装置の概略縦断面図である。本実施例の装置では、シリコン原料となるオクタメチルシクロテトラシロキサン(以下OMCTSと呼ぶ。化学式は、Si<sub>4</sub>O<sub>12</sub>C<sub>8</sub>H<sub>24</sub>である。)ガスは、この図では表されていないOMCTSタンクから供給される、液体状のOM

CTSを、マスフロー型の液体流量調節器255で流量調節し、蒸発器265で完全に気化させ、流量調節器256で流量調節された窒素ガスと混合されて生成される。オゾン含有酸素は、流量調節器254で流量調節された酸素ガスを無声放電型のオゾン発生器264に導入し、0.1~1.0%のオゾンを含ませて生成される。また、アンモニアガスは、この図では表されていないHN<sub>3</sub>ガスボンベから供給され、流量調整器257で流量調節される。このようにして生成されたOMCTSガス、オゾン含有酸素ガスおよびアンモニアガスは、OMCTS導入口267、オゾン導入口268およびNH<sub>3</sub>導入口266からマニホールド269に導入される。マニホールド内では、これらのガスは混合され、ガス拡散板271に当たる事によって、ほぼ均一に拡散する。さらに、シャワー電極273に当たると、さらに均一に分散し、基板275の表面に吹き付けられる。基板275は、SiCサセプタ276上に装着され、石英板277を通して加熱ランプ278から光加熱され、200~450℃程度の温度に保持されている。排気管279は真空ポンプ281に接続されており、反応室274の内部の圧力は、0.1~数十Torrの適当な値に保持されている。シャワー電極273は、絶縁リング272によって他の部分と電気的に絶縁されており、RF発生器286で発生される13.56MHzの高周波が印加されている。このRF発生器286の出力は、パルス発生器287で発生されるパルスによって制御されており、周期的にON・OFFしたり、強度が変化したりする。

【0058】本実施例では、以上の様な装置を用いて、成膜温度300℃、成膜圧力1.0Torr、RF周波数13.56MHz、RFパワー300W、パルス周波数0.2Hz(パルス周期5秒)、デューティー比D=20%、OMCTS流量50SCCM、酸素(O<sub>2</sub>)流量0.1SLM、オゾン濃度1%、アンモニア(NH<sub>3</sub>)流量1.0SLMの成膜条件で絶縁膜を形成した。

【0059】結果として約1200オングストローム/minの膜成長速度が得られ、ステップカバレージは、90%以上であった。また、その組成は、窒素含有率が5~25%のSiONであり、膜中水分量も1%以下で、良好な絶縁膜である事が判った。

【0060】本実施例の絶縁膜の成膜機構は以下のように説明される。まず、RFパワーがOFFの状態、オゾンとOMCTSの熱CVD反応が行われる。この反応で形成されるのは、水分をかなり多く含んだSiO<sub>2</sub>膜である。次に、RFパワーがONになると、アンモニアプラズマが発生する。熱CVD反応で形成されたSiO<sub>2</sub>膜は、このアンモニアプラズマに曝されると窒素イオンが注入され、窒化されるものと考えられる。RFパワーがONの時間は、同時にプラズマCVD反応も生じており、反応ガス中にSi、O、N、Hが含まれるのでS

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ION膜が形成される。本実施例では、オゾンとOMCTSの熱CVD反応のデポレートが約1000オングストローム/min、RFパワーをONにしたプラズマCVD反応のデポレートが2000オングストローム/minであり、RFパワーOFFの時間が4秒であるので、約125オングストロームの膜厚のSiO<sub>2</sub>膜をアンモニアプラズマに曝した事になる。本発明の発明者は、この程度の膜厚のSiO<sub>2</sub>膜が、アンモニアプラズマで容易に窒化される事を確認しており、しかも、RFパワーのON・OFFにより、膜厚方向に組成分布や膜質分布がほとんど生じない事も確認している。

【0061】尚、本実施例では、RF発振器の周波数として13.56MHzを用いたが、本発明の実施例1と同様に、450Hz等の低周波を加えるとさらに良い結果が得られる。また、本実施例では、パルス発生器を用いてRFパワーのON・OFFを行ったが、図6の様な装置を用いて、プラズマの照射・非照射の状態を繰り返しても同様の結果が得られる。また、本実施例では、有機シランガスとして、オクタメチルシクロテトラシロキサン(OMCTS)を用いたが、珪酸エチル(TEOS: Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>)、テトラメチルシラン(TMS: Si(CH<sub>3</sub>)<sub>4</sub>)、テトラメチルシクロテトラシロキサン(TMCTS)、ヘキサメチルジシラザン(HMDS)、トリエトキシシラン(SiH(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)等のシリコン含有化合物を用いても同様の結果が得られる。また、有機シランガスとして、トリスジメチルアミノシラン(SiH(N(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>)やトリスジエチルアミノシラン(SiH(N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>)<sub>3</sub>)など、Si-N結合を有する化合物を用いると、窒素含有率を上げる事が出来る。また、本実施例では窒素を注入するプラズマを発生させるガスとして、アンモニア(NH<sub>3</sub>)を用いたが、N<sub>2</sub>やN<sub>2</sub>とH<sub>2</sub>の混合ガスなどでも同様の効果が得られる。

【0062】図19は、本発明の第9の実施例のプラズマ化学気相成長装置の概略を表す縦断面図である。

【0063】イオン源空洞305には、流量調節器288で流量調節されたアンモニアガスNH<sub>3</sub>と、流量調節器289で流量調節された笑気ガスN<sub>2</sub>Oと、流量調節器290で流量調節された窒素ガスN<sub>2</sub>が供給され、圧力は、p=100mTorrに保たれている。また、マイクロ波電源300から、導波管299及び透過窓298を経由して、周波数2.45GHzのマイクロ波が供給されている。さらに、主電磁石コイル303の作る875ガウスの磁場によって、イオン源空洞305内では電子サイクロトロン共鳴(ECR)が起こっており、イオン化率の高いプラズマが発生する。ここで生成される酸素イオン、窒素イオン、水素イオンは主電磁石303の発散磁界及び補助コイル1.304によって反応室309へ引き出され、グリッド307の隙間を通り抜けて、基板310へ照射される。グリッド307は、印加

する電圧によってイオンを跳ね返したり、通過させたりするシャッターの役目をしている。

【0064】シリコン原料となるTDEASガスは、80℃に保たれた恒温容器317内に保温されたTDEAS(液体)318から蒸発したTDEASガスを、流量調節器292で流量調節し、流量調節器291で流量調節された窒素ガスと混合されて、ソースガス導入口308から反応室へ導入され、基板表面へ吹き付けられる。ここで、TDEAS318の入っている恒温容器317からソースガス導入口308につながる配管とソースガス導入口308は、80℃以上の一定温度に保たれている。基板310は、サセプター312上に装着され、ヒーター315によって300℃に加熱されている。また、反応室の圧力は、真空ポンプ316によって、約1mTorrに保たれている。

【0065】本実施例のプラズマCVD装置では、まず、マイクロ波電源300を動作させ、主電磁石コイルにより875ガウスの磁場を発生させ、ECR共鳴を生じさせて、イオン源空洞305内に窒素ガス、アンモニアガス、および、笑気ガスからなるプラズマを発生させる。補助コイル1.304および補助コイル2.311に流す電流は、イオン源から基板に向かう磁場を発生させる向きで小さな値にしておき、プラズマの照射が均一になる程度にしておく。また、グリッド307には正の電圧を印加して、プラズマ中に存在する、酸素イオンO<sup>+</sup>、窒素イオンN<sup>+</sup>、水素イオンH<sup>+</sup>などの正に帯電したイオンが、正の電界によって反跳され、基板310に照射されないようにしておく。この状態では、基板310表面には、イオン源空洞305内のプラズマ中で生成された中性の活性種(ラジカル)や分子のみが供給される。ここで、TDEASガスを供給すると、中性活性種(ラジカル)により活性化された熱化学反応が起こり、ステップカバレッジの良いSiON膜が形成される。本実施例では、この熱化学反応によるSiON膜を約10nm形成した。次に、グリッド307に印加する電圧をゼロあるいは負の小さな値にし、正に帯電したイオンが、基板310の表面に照射されるようにする。すると、熱化学反応で形成されたSiON膜は、イオン衝撃を受ける事により膜中の水分や炭素が脱離し、プラズマCVD膜と同等の膜質を有する、膜質の良いSiON膜となる。また、基板表面ではプラズマ化学反応も起こっており、プラズマCVD・SiON膜も同時に形成される。そこで、グリッド307に印加する電圧を、1秒から10秒程度の周期で変化させると、基板310に照射されるイオン数が周期的に変化し、熱化学反応による熱CVD・SiON膜の形成と、プラズマCVD・SiON膜への改質が交互に行われる事になる。その結果、ステップカバレッジ及び段差埋め込み正に優れたプラズマCVD・SiON膜が形成される。特に本実施例では、反応室圧力を1mTorr程度にしているため、アスペ

クト比の大きな溝の埋め込みも可能である。

【0066】尚、基板310に照射されるイオンを変化させる手段として、上記の例ではグリッド307に正電圧を印加する事による反跳電界を用いたが、補助コイル1・304によるミラー型磁場や、補助コイル2・311によって形成されるカスプ型磁場や、バイアス印加電源313からサセプター312に正の電圧を印加して形成される反跳電場を用いても良い。また、図19には示されていないが、機械的なシャッターを用いても同様の結果が得られる。但し、機械的なシャッター等を用いて、ラジカルの拡散を妨げるような構造にした場合には、ラジカル発生器を用いて基板近傍にラジカルを供給し、熱化学気相成長を促進し、熱CVD膜の成長を促進するようにした方がよいのは言うまでもない。

【0067】また、上記実施例では、イオン源として電子サイクロトロン共鳴型(ECR)イオン源を用いたが、イオンの強度を変化させる事が出来れば、その形式によらず同様の結果が得られる。

【0068】また、本実施例では、有機シランガスとして、トリスジエチルアミノシラン(TDEAS:化学式 $\text{Si}(\text{H}(\text{N}(\text{C}_2\text{H}_5)_2)_3)$ )を用いたが、珪酸エチル(TEOS:化学式 $\text{Si}(\text{OC}_2\text{H}_5)_4$ )、テトラメチルシラン(TMS:化学式 $\text{Si}(\text{CH}_3)_4$ )、テトラメチルシクロテトラシロキサン(TMCTS)、オクタメチルシクロテトラシロキサン(OMCTS)、ヘキサメチルジシラザン(HMDS)、トリエトキシシラン(化学式 $\text{Si}(\text{H}(\text{OC}_2\text{H}_5)_3)$ )、トリスジメチルアミノシラン(化学式 $\text{Si}(\text{H}(\text{N}(\text{CH}_3)_2)_3)$ )等のシリコン含有化合物を用いても同様の結果が得られる。

【0069】さらに、反応ガス中に、シラン等のシリコン無機化合物やアンモニア等窒素化合物や、リン、ホウ素、砒素、アンチモン等の水素化合物や有機化合物を混入させた場合にも同様の結果が得られる。また、本実施例では、プラズマを発生させるガスとして、アンモニア( $\text{NH}_3$ )を用いたが、 $\text{N}_2$ や $\text{N}_2$ と $\text{H}_2$ の混合ガスなどでも同様の効果が得られる。

【0070】

【発明の効果】以上説明したように本発明の化学気相成長法は、基板表面へのプラズマ照射強度を周期的に変化させながら、優れたステップカバレージを持つオゾンとTEOSの熱CVD膜の形成と、その熱CVD膜のプラズマCVD膜と同等な膜質への改質、および、プラズマTEOS・CVD膜の形成を繰り返して行うため、微細でアスペクト比の大きい溝を埋め込む事が可能なほど優秀なステップカバレージを有し、膜中水分量や膜中ストレスが小さく、良好な膜質を有するプラズマCVD膜の形成が可能になる効果がある。また、本発明の化学気相成長法は、原料ガスとして、有機シランとオゾンの他に、過酸化水素等の添加ガスを含むため、埋め込み性お

よびフロー性の優れた絶縁膜の形成が可能になる。

【0071】また、本発明の化学気相成長装置は、有機シランを供給する機構と、酸素或いはオゾン含有酸素を供給する機構と、プラズマ発生強度を周期的に変化させる機構、或いは、1つの反応容器内に設けられたプラズマ強度の異なる複数のプラズマ照射機構と、この複数のプラズマ照射機構の間で基板を移動させる機構、或いは、プラズマ照射強度を周期的に変化させるための機械的或いは電磁的なシャッターとを有しているため、本発明のプラズマ化学気相成長法を効果的に実現できる。また、本発明の化学気相成長装置は、過酸化水素、水素、水、炭化水素、アルコール、カルボニル化合物、カルボン酸の内の少なくとも1種類をガス状態にして供給する機構とを有しており、本発明の化学気相成長法を効果的に実現できる。

【0072】また、本発明の多層配線の製造方法は、有機シランと酸素或いはオゾンと過酸化水素等の添加ガスを原料とする本発明記載の化学気相成長法を用いるか、あるいは、有機シランと酸素或いはオゾンを原料ガスとし、基板表面へのプラズマ照射強度を周期的に変化させる、本発明記載のプラズマ化学気相成長法を用い、金属配線間に靱(ボイド)の発生のない絶縁膜を、金属配線の高さ以上の膜厚だけ形成する工程を含むため、シリカ塗布膜を用いる従来の多層配線の製造方法に比べ、層間膜中の水分量が大幅に減少し、耐クラック性の向上、ストレスマイグレーションの低減、スルーホールの導通特性の向上等が図られる。また、本発明の多層配線の製造方法の工程数は、従来の方法に比べて著しく減少しているので、歩留りが向上し、コストが低減されるという効果がある。

【図面の簡単な説明】

【図1】本発明の第1の実施例を表すプラズマ化学気相成長装置の概略縦断面図。

【図2】図1のプラズマ化学気相成長装置の動作を、印加高周波電力、酸素イオン数、オゾン濃度の時間変化について表す図。

【図3】本発明の原理の概略を表すモデル図。

【図4】図2のような動作を行った際の、時間経過と膜の成長過程を表す縦断面図。

【図5】図2のような動作を行った際の、高周波オン時間( $t_{\text{ON}}$ )の割合(デューティD)と膜成長速度、ステップカバレージ、OH基の吸収係数の関係図。

【図6】本発明の第2の実施例2のプラズマ化学気相成長装置の反応室の概略平面図及び縦断面図。

【図7】本発明の第3の実施例のプラズマ化学気相成長装置の概略を表す縦断面図。

【図8】本発明の第4の実施例のアルミ多層配線の層間絶縁膜平坦化法を表す縦断面図。

【図9】従来のプラズマ気相成長装置の概略図。

【図10】プラズマ化学気相成長法と、オゾンとTEO

Sの熱化学気相成長法とを交互に作用する従来の方法における、シャワー電極に印加される高周波電力と、プラズマ中の酸素イオン数と、原料ガス中のオゾン濃度の、成膜時間に対する変化図。

【図11】プラズマ化学気相成長法とオゾン熱化学気相成長法を交互に行った場合の膜成長を表す縦断面図。

【図12】プラズマ化学気相成長法とシリカ塗布法を用いた、従来の多層配線用平坦化絶縁膜の形成方法を示す縦断面図。

【図13】図1の第1の実施例のプラズマ化学気相成長装置を使用した、第5の実施例の動作の方法を示す高周波電力等の時間変化図。

【図14】本発明の第6の実施例のプラズマ化学気相成長装置の概略を表す縦断面図。

【図15】本発明の第7の実施例のプラズマ化学気相成長装置の概略を表す縦断面図。

【図16】本発明の第6の実施例のプラズマ気相成長法を用いて形成された絶縁膜のステップカバレッジを表す縦断面図。

【図17】本発明の第7の実施例のプラズマ気相成長法を用いて形成された絶縁膜のステップカバレッジを表す縦断面図。

【図18】本発明の第8の実施例のプラズマ化学気相成長装置の概略を表す縦断面図。

【図19】本発明の第9の実施例のプラズマ化学気相成長装置の概略を表す縦断面図。

【符号の説明】

1、2 流量調節器

3 液体流量調節器

4、5 流量調節器

6～10 バルブ

11 オゾン発生器

12 蒸発器

13 オゾン導入口

14 TEOS導入口

15 マニホールド

16 He導入口

17 ガス拡散板

18 絶縁リング

19 シャワー電極

20 反応室

21 SiCサセプター

22 石英板

23 加熱ランプ

24 排気管

25 バタフライバルブ

26 真空ポンプ

27 パルスモーター

28 基板

29 温度センサー

30 圧力センサー

31 バルブ開度調節器

32 加熱ランプコントローラー

33 プリアンプ

34 プリアンプ

35 ローパスフィルター

36 450kHz高周波電源

37 マッチングボックス

38 ハイパスフィルター

39 13.56MHz高周波電源

40 パルスジェネレーター

41 プロセスコントローラー

42 オゾン分子数の変化

43 酸素イオン数の変化

44 高周波電力の変化

45 電子

46 TEOS解離分子

47 酸素イオン

48 酸素イオンのドリフト

49 TEOS解離分子の拡散

50 膜形成前駆体

51 形成膜

52 基板

53 TEOSの拡散

54 TEOS

55 酸素ラジカル

56 オゾン分子

57 酸素ラジカルの拡散

58 オゾン分子の拡散

59 膜形成前駆体擬液体層

60 第1のプラズマCVD膜

61 アルミ配線

62 第1の熱CVD膜

63 第2のプラズマCVD膜

64 第2のプラズマCVD膜成長前の形成膜

65 第2の熱CVD膜

66 第2のプラズマCVD膜成長後の形成膜

67 第3のプラズマCVD膜

68 第3のプラズマCVD膜成長前の形成膜

69 基板

70 熱CVD領域

71 サセプター

72 反応室

73 TEOS導入口

74 酸素導入口

75 オゾン導入口

76 絶縁体

77 RF導入端子

78 シャワー電極

79 回転軸

30

40

50

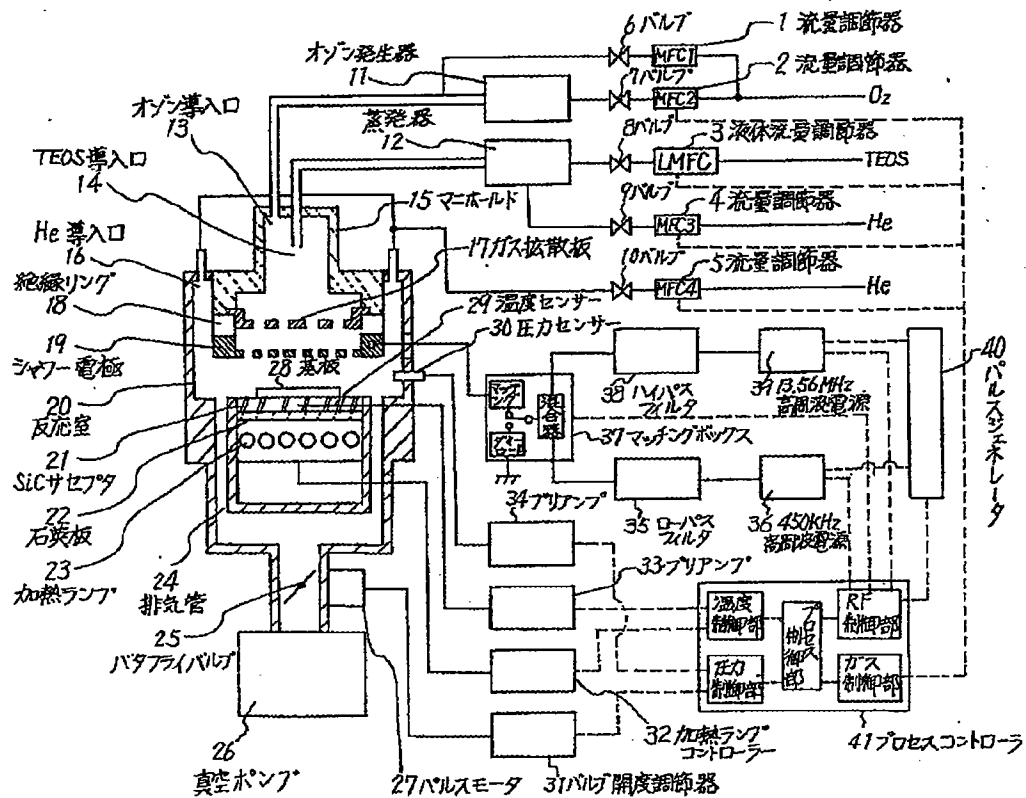
80	ヒーター	126	バルブ
81	シャワーインjekター	127	バルブ
82	絶縁リング	128	流量調節器
83	ガス分散板	129	13.56MHz高周波電源
166	プラズマCVD領域	130	ハイパスフィルター
84	マイクロ波電源	131	TEOS
85	導波管	132	バブラー
86	透過窓	133	450kHz高周波電源
87	流量調整器	134	ローパスフィルター
88	流量調整器	10 135	マッチングボックス
89	バルブ	136	マニホールド
90	バルブ	137	酸素・オゾン導入口
91	Ar導入口	138	TEOS導入口
92	O <sub>2</sub> 導入口	139	He導入口
93	イオン源空洞	140	ガス拡散板
94, 94'	主電磁石コイル	141	絶縁リング
95	反応室	142	シャワー電極
96, 96'	補助コイル	143	反応室
97	オゾン導入口	144	SiCサセプター
98	オゾン発生器	20 145	石英板
99	バルブ	146	加熱ランプ
100	バルブ	147	基板
101	流量調節器	148	排気管
102, 102'	反射磁石コイル	149	真空ポンプ
103	流量調節器	165	オゾン発生器
104	排気管	150	オゾン濃度の時間変化
105	真空ポンプ	151	酸素イオン数の変化
106	基板	152	高周波電力の変化
107	TEOS導入口	153	アルミ配線
108	Ar導入口	30 154	第1のプラズマCVD膜
109	サセプター	155	第1の熱CVD膜
110	ヒーター	156	第2のプラズマCVD膜
111	TEOS	158	アルミ配線
112	恒温容器	159	プラズマCVD膜
113	流量調節器	160	シリカ塗布膜(1回塗布)
164	コイル駆動電源	161	シリカ塗布膜(複数回塗布)
168	バイアス印加装置	162	エッチバック後シリカ塗布膜
114	アルミ配線	163	プラズマCVD膜
115	基板	169	13.56MHz高周波電力の変化
167	本発明のCVD膜(途中経過)	40 170	450kHz高周波電力の変化
116	本発明のCVD膜	171	イオン電流密度の変化
117	レジスト	172	平均イオンエネルギーの変化
118	平坦化された層間膜	173	成長速度の変化
119	流量調整器	174	流量調節器
120	流量調整器	175	液体流量調節器
121	バルブ	176~178	流量調節器
122	バルブ	179~183	バルブ
123	流量調整器	184	恒温容器
124	バルブ	185	過酸化水素(H <sub>2</sub> O <sub>2</sub> )
125	流量調節器	50 186	オゾン発生器



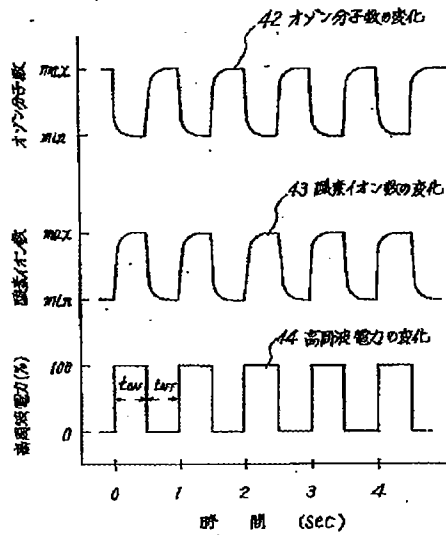
187	蒸発器	243	基板
188	オゾン導入口	244	マニホールド
189	TEOS導入口	245	アルミ配線
190	H <sub>2</sub> O <sub>2</sub> 導入口	246	TEOS/O <sub>2</sub> 系CVD膜
191	He導入口	247	本実施例の絶縁膜 (H <sub>2</sub> O <sub>2</sub> 流量=0SCC M)
192	ガス拡散板	248	本実施例の絶縁膜 (H <sub>2</sub> O <sub>2</sub> 流量=5SCC M)
193	絶縁リング	249	ボイド (鬆)
194	シャワー電極	10 250	基板
195	反応室	251	アルミ配線
196	SiCサセプター	252	本実施例の絶縁膜
197	石英板	253	基板
198	加熱ランプ	254	流量調節器
199	排気管	255	液体流量調節器
200	バタフライバルブ	256~258	流量調節器
201	真空ポンプ	259~263	バルブ
202	パルスモーター	264	オゾン発生器
203	バルブ開度調節器	265	蒸発器
204	圧力センサー	20 266	NH <sub>3</sub> 導入口
205	プリアンプ	267	OMCTS導入口
206	RF発振器	268	オゾン導入口
207	基板	269	マニホールド
208	マニホールド	270	N <sub>2</sub> 導入口
209	流量調節器	271	ガス拡散板
210	液体流量調節器	272	絶縁リング
211~213	流量調節器	273	シャワー電極
214~218	バルブ	274	反応室
219	恒温容器	275	基板
220	過酸化水素 (H <sub>2</sub> O <sub>2</sub> )	30 276	SiCサセプター
221	オゾン発生器	277	石英板
222	蒸発器	278	加熱ランプ
223	オゾン導入口	279	排気管
224	TEOS導入口	280	バタフライバルブ
225	H <sub>2</sub> O <sub>2</sub> 導入口	281	真空ポンプ
226	He導入口	282	パルスモーター
227	ガス拡散板	283	バルブ開度調節器
228	絶縁リング	284	圧力センサ
229	シャワー電極	285	プリアンプ
230	反応室	40 286	RF発振器
231	SiCサセプター	287	パルス発生器
232	石英板	288~292	流量調節器
233	加熱ランプ	293~297	バルブ
234	排気管	298	透過窓
235	バタフライバルブ	299	導波管
236	真空ポンプ	300	マイクロ波電源
237	パルスモーター	301	N <sub>2</sub> 導入口
238	バルブ開度調節器	302	NH <sub>3</sub> , N <sub>2</sub> O導入口
239	圧力センサー	303	主磁石コイル
240	プリアンプ	50 304	補助コイル1
241	RF発振器		
242	パルス発生器		

- |     |            |     |          |
|-----|------------|-----|----------|
| 305 | イオン源空洞     | 312 | サセプタ     |
| 306 | グリッド電圧制御電源 | 313 | バイアス印加電源 |
| 307 | グリッド       | 314 | 排気管      |
| 308 | ソースガス導入口   | 315 | ヒーター     |
| 309 | 反応室        | 316 | 真空ポンプ    |
| 310 | 基板         | 317 | 恒温容器     |
| 311 | 補助コイル2     | 318 | TDEAS    |

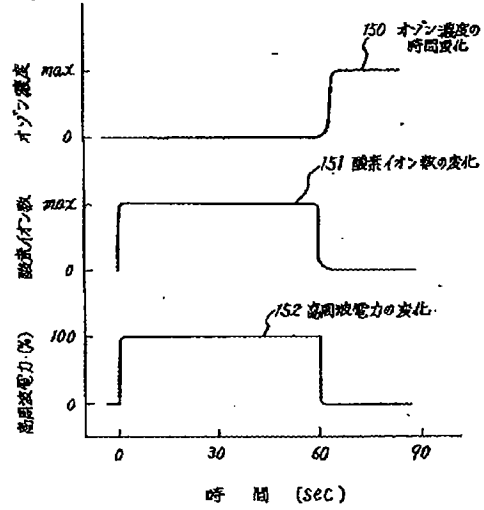
【図1】



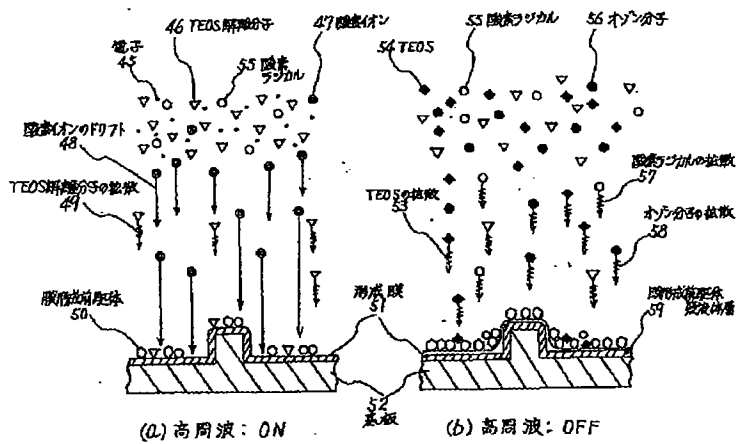
【図2】



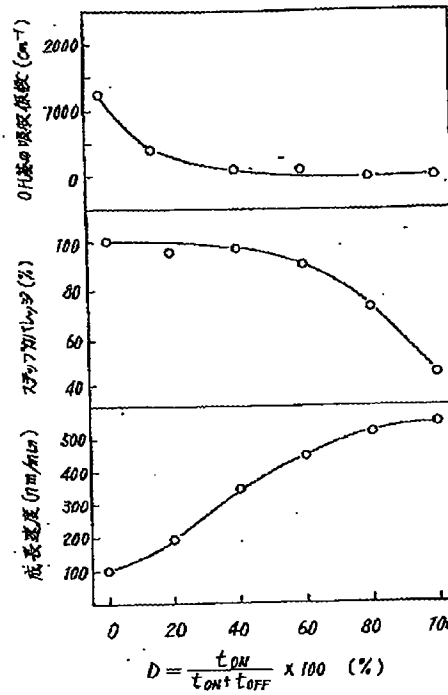
【図10】



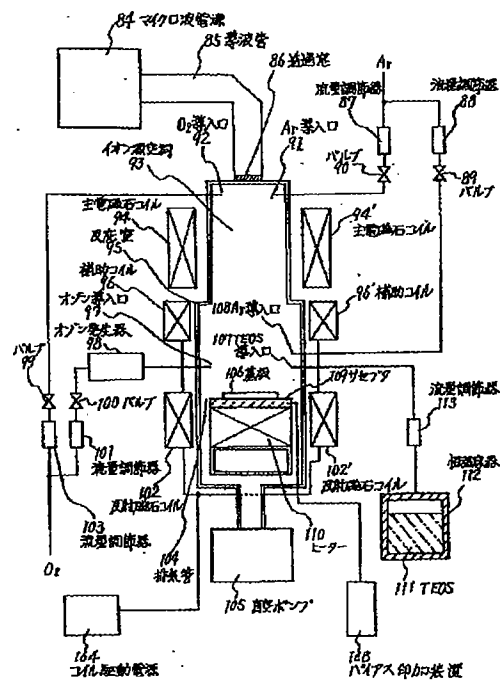
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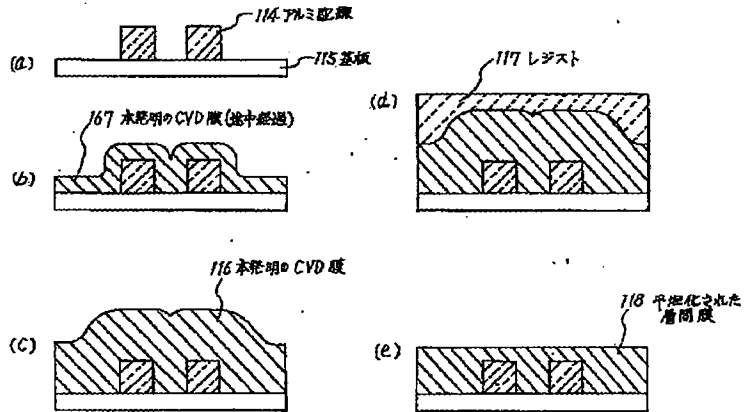
【圖 5】



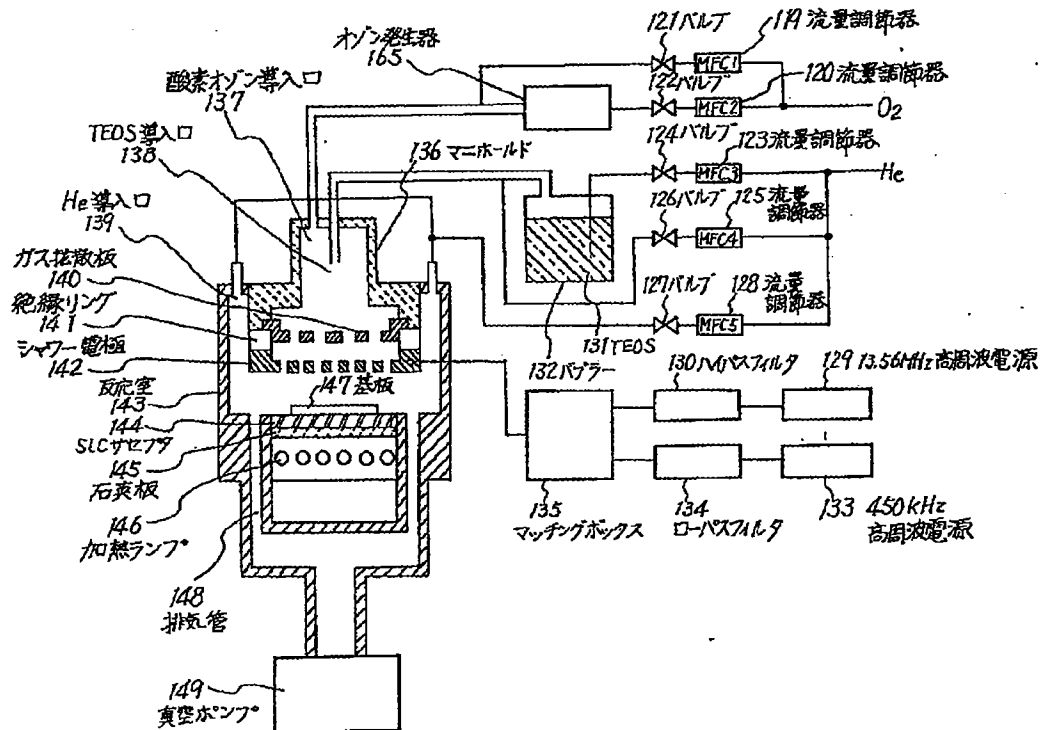
【図7】



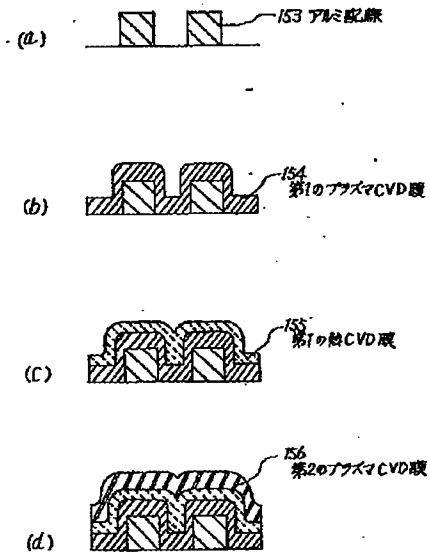
【図8】



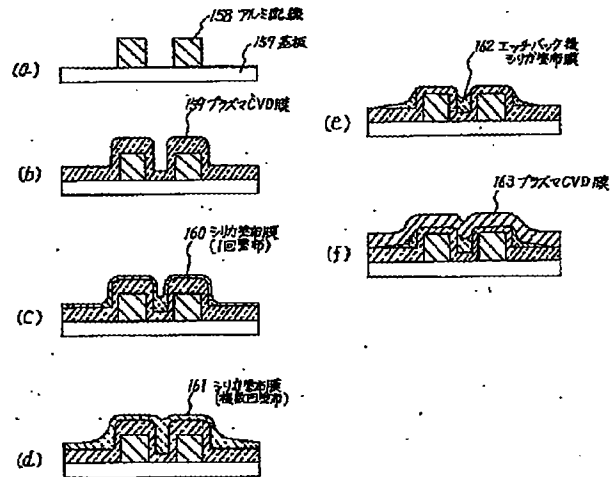
【図9】



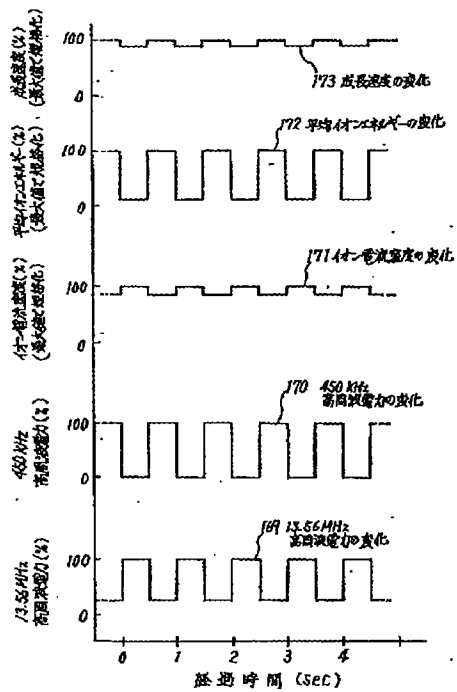
【図11】



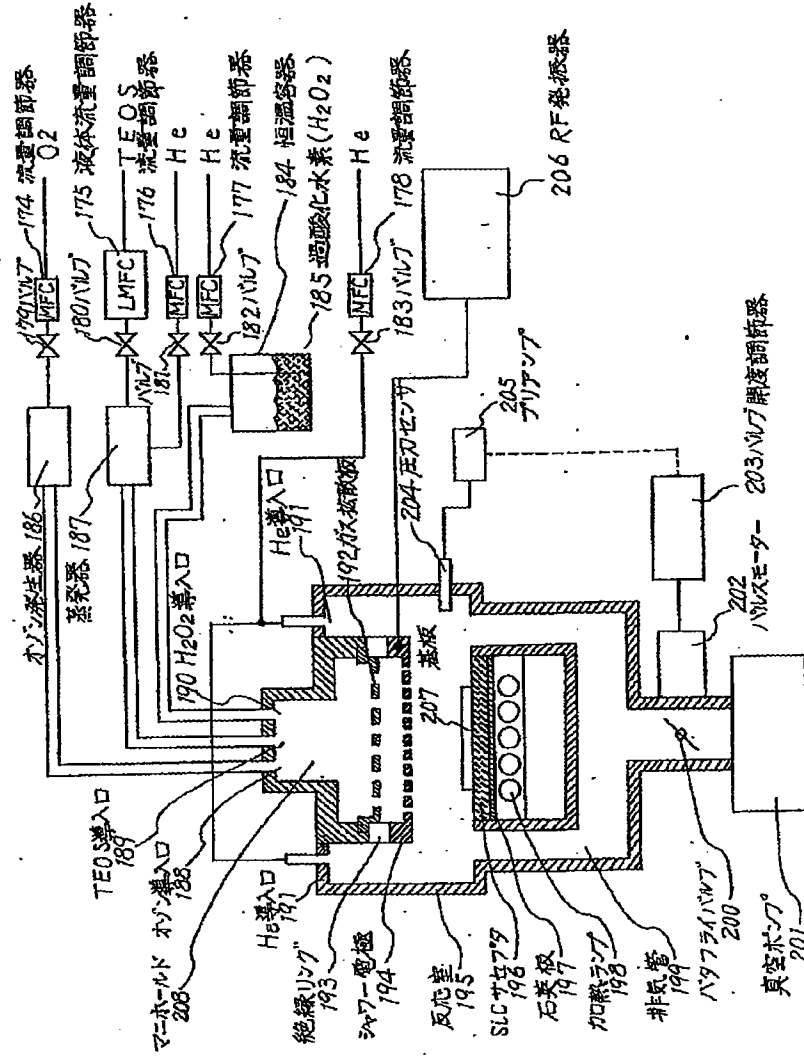
【図12】



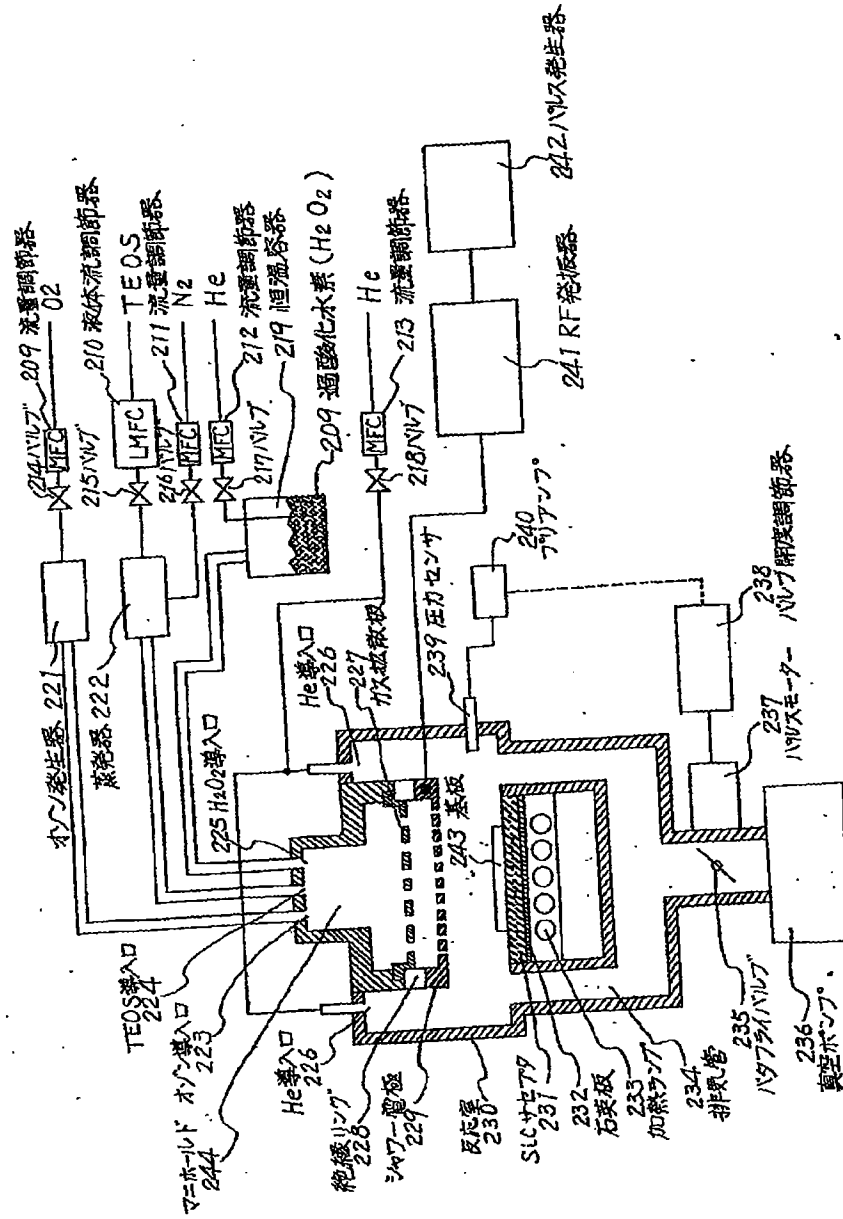
【図13】



【図14】

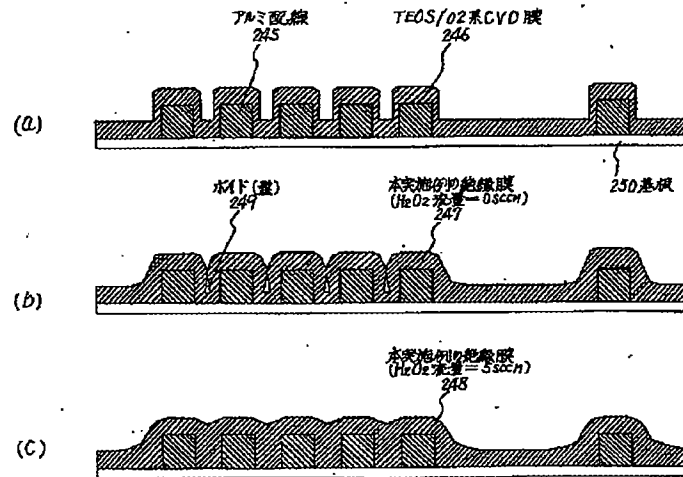


【圖 15】

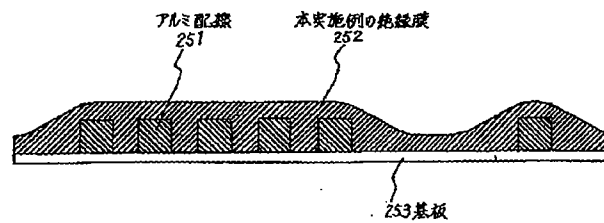




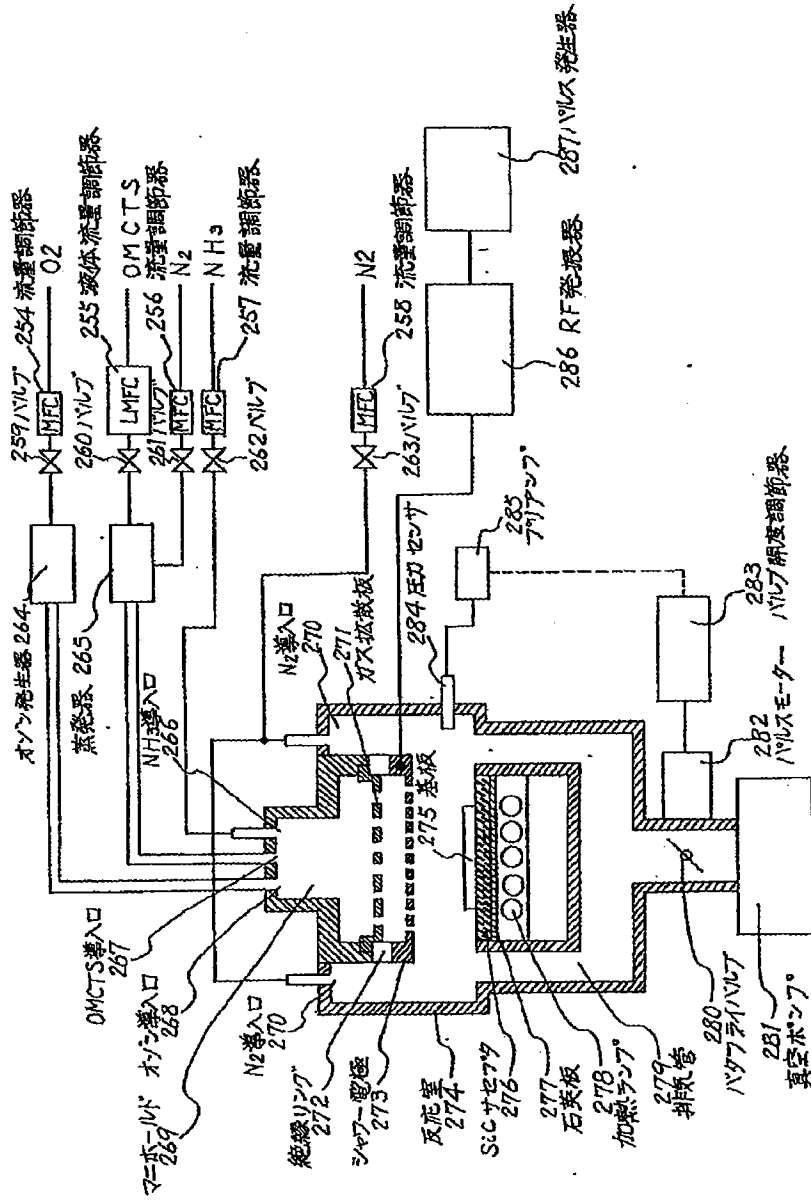
【図16】



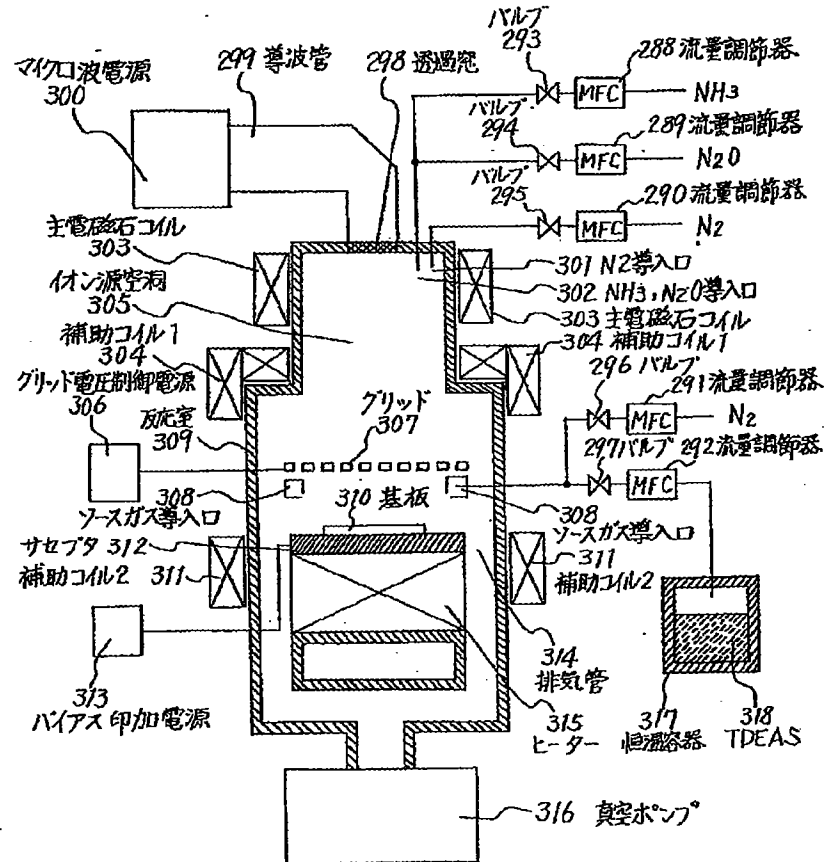
【図17】



【図18】



【図19】



フロントページの続き

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技術表示箇所